APPENDIX 4

MUD LAKE ARUM EXPERIMENT
and
BIOGEOCHEMICAL BARRIERS IN MINE WASTE RESTORATION - AN ECOLOGICAL ENGINEERING APPROACH, KALIN ET AL.
and
PASSIVE TREATMENT PROCESSES FOR THE MINERAL SECTOR, KALIN ET AL.

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Mud Lake ARUM Experiment

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SUMMARY

Groundwater with a low pH and contaminated with heavy metals is entering Mud Lake. This water body has been identified as the best site to treat this water before it enters Confederation Lake. Biological treatment using ARUM (Acid Reduction Using Microbiology) is the suggested treatment method.

A laboratory experiment was carried out to determine whether ARUM can remove Zn and other contaminants from Mud Lake water. A preliminary experiment was carried out to determine what would happen to the groundwater in oxidising conditions. Such conditions will be present in the mixed surface waters of Mud Lake. This experiment sought to determine whether, to what extent and at what rate Fe oxidation and subsequent precipitation of $Fe(OH)_3$ can occur.

This experiment determined that aeration of groundwater entering Mud Lake (GD trap water) at room temperature (similar to summer conditions in the field) results in oxidation, hydrolysis and precipitation of Fe commencing at 88 h. From around 213 h, an equilibrium between Fe^{2+} and Fe^{3+} is attained with no further net oxidation or removal of Fe from solution. Oxidation rate was estimated as around 103 $mg.m^{-3}.min^{-1}$ and was little influenced by the presence of a sediment. However, in the presence of sediment approximately 50 % of the Fe and acidity in the water was removed in 27 days.

In cold room conditions, where the temperature (1-5°C) is similar to what would be encountered within and just above sediments in the field in winter, oxidation did not occur during the first 27 day period of observations with all Fe remaining in the Fe2+ state. However, within 72 days oxidation had commenced in jars with sediment and pH had declined to <3. As at room temperature, *50* % of the acidity and Fe was removed by the sediment.

ARUM worked very well on groundwater entering Mud Lake (GD trap water). Within 23 days at room temperature, dissolved Zn concentration was reduced from >80 $mg.L^{-1}$ to <1 $mg.L^{-1}$ in reducing condition induced through addition of decomposable organic matter (alfalfa or potato waste). With added alfalfa some of the Zn remained in the suspended solid fraction. This is potentially mobile. With potato waste, the Zn was almost totally removed to the sediment. Therefore, potato waste is the amendment of choice. In cold room conditions, and in the presence of an amendment and Mud Lake sediment, reducing conditions were established in Mud Lake groundwater within 54 days and Zn concentration reduced to 0.334 $mg.L^{-1}$ in the presence of potato waste.

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10 INTRODUCTION

Contaminated groundwater started entering Mud Lake in the spring of **1994.** This lake is shallow and contains deep organic sediments, suitable conditions for the application of biological treatment with ARUM.

In order to determine the potential of oxidation and ARUM to treat Mud Lake water in different conditions, laboratory tests are required.

In Section ***2,*** an oxidation experiment is described where groundwater entering Mud Lake was aerated in jars with or without the presence of a sediment in both room temperature and cold room conditons which reflect field conditions in high summer and in winter, under the ice respectively. Aeration maintained saturated oxygen concentration and therefore provides an idea of the maximum oxidation rates expected in the field with wind driven water mixing.

In Section 3, an ARUM experiment is described where the effect of adding decomposable organic wastes (potato waste and alfalfa) to jars containing Mud Lake sediment and groundwater entering the lake. This experiment was designed to determine whether dissolved metals and acidity could be removed from the water column in reducing conditions.

The results of these experiments are used to develop design criteria for a scale-up in the field in the summer of **1995** (Section 5).

2.0 OXIDATION TEST

2.1 Methodology

Jars were set up with 1.7 L of GD trap water (contaminated groundwater entering Mud Lake) or 0.85 L of sediment made up to 1.7 L with GD trap water. The water and sediment were collected from under the ice in December, 1994. The jars were aerated to maintain near saturated dissolved oxygen concentration. Jars were kept in the laboratory (18-22 "C) or placed in the cold room (1-5 "C). Eh, conductivity, pH and temperature were monitored.

Results are shown for one jar of each treatment (Jars 1, 4, 6 and 9 as used for the titration). Results from other jars follow the same patterns. Samples from one jar of each treatment were titrated against 0.01 N NaOH with the Metrohm Titrino autotitrator to determine acidity and from the slope of the plot, the oxidation state of the water.

2.2 Results

pH (Fig. 1): At the first measurement, 1 h after set-up, pH values were in the range 5.0 to 5.5. At room temperature pH exhibited a rapid decline to 3.6 (water only) and 3.94 (water and sediment) over a 40 h period. Thereafter, pH declined at a fairly steady rate until 6.5 days after which steady values in the range 2.2-2.5 were found for the duration of the observations. In the cold room jars, pH declined to 4.12 (water only) and 4.49 (water and sediment) after which values remained fairly steady between 4 and 4.5. Throughout the period of observations, pH values were slightly lower in the absence of a sediment in both temperature regimes, indicating that the sediment has some pH-buffering capacity. The steady low values attained at room temperature indicate that the lowest pH likely to occur in Mud Lake is around 2.2-2.5.

Eh (Fig. 2): Eh values rose from initial conditions (300-370 mV) in all conditions. At room temperature, values rose steadily to around +650-700 mV at 6.5 days with or without the presence of a sediment. After this time, values remained in the 650-750 mV range. In the cold room, Eh rose to 400-450 mV by 2.5 days. After this time, values rose very slowly to around 475 mV at 15.5 days. The presence of a sediment had very little effect on Eh values in the cold room conditions.

Conductivity (Fig. 3): Following a slight initial decline, conductivity values were stable in both temperature regimes and in the presence or absence of a sediment from 15 h to 15.5 days after set-up. In the presence of a sediment, values were generally a little lower, both in the cold room and at room temperature, indicating a greater net removal of dissolved substances. All values were in the 3000 to 4000 $\mu mho.cm^{-1}$ range which is probably the highest likely to be encountered in Mud Lake.

Acidity (Fig. *4*): Acidity values, in $mg.L^{-1}$ equivalent of $CaCO_3$, were obtained from the titration with NaOH. From the initial readings 1 h after set-up, acidities were much higher in the absence of a sediment. Acidities remained in the range 1800-2220 $mg.L^{-1}$ in jars with water only at both temperatures. In the presence of a sediment, there was a substantial decline from around 1700 $mg.L^{-1}$ initially to 1000-1100 $mg.L^{-1}$ in 6.5 days at room temperature and 15.5 days in the cold room. Initial rates of decline were similar at the 2 temperatures indicating the involvement of similar removal mechanisms during this period. Clearly, sediments are able to remove a substantial proportion (nearly 50 %) of the total acidity from the **GD** trap water. It should be noted that the acidity decline was not associated with a conductivity decline suggesting a net removal of acid contributing factors (e.g. H^+, Fe^{2+}, Fe^{3+} and Zn^{2+}) by the sediments. The total acidity removal was similar at the two temperatures but the rate did show some temperature dependence at least in the late stages.

Titration curves (Fig. 5a-5h): Titration curves for the 112 h following set-up are shown in Fig. 5a to 5d. At room temperature the water only samples (Fig. 5a) showed a decline

in initial pH. However, the overall shape of the curves was remarkably constant up to and including 88 h with a long plateau at a pH between 5.5 and 8 which represents the zone in which Fe^{2+} precipitates with the OH^- in the titrant. The length of this plateau is a measure of the Fe^{2+} content of the sample. At 112 h, there was a short plateau between pH 3 and **4,** where Fe^{3+} precipitates. This indicates that by 112 h, Fe^{3+} was present in the water. In other words, Fe^{2+} oxidation had commenced. In the presence of a sediment (Fig. 5b), there was a considerable decrease in the length of the 'Fe^{2+} plateau' contributing to the reduction in total acidity. As with the water-only jar, there were the first indications of Fe^{2+} oxidation at 112 h.

In the cold room, the shapes of the curves for the 'water only' jar remained very similar over the 112 h (Fig. 5c) and were also similar in shape to those for the room temperature jar. There were no indications of Fe^{3+} oxidation in this period. In the presence of a sediment, there was a reduction in length of the Fe^{2+} plateau as observed at room temperature (Fig. 5d). Again there was no indication of Fe^{3+} oxidation.

Titration curves for the 5.5 to 15.5 days following set-up are shown in Fig. 5e-5h. There was an increase in the Fe^{3+} plateau and associated decrease in the Fe^{2+} plateau up to 9 days. Thereafter, there was no further increase in the Fe^{3+} plateau:Fe^{2+} plateau ratio. Indicating that there was no further net Fe^{2+} oxidation after this time. In other words, a fairly stable equilibrium was established with Fe^{2+} oxidation rate balanced by Fe^{3+} reduction rate. A substantial proportion of the dissolved Fe remains in the reduced state. In the presence of a sediment (Fig 59, removal of acidity continued until 165 h after set up. From this time on, the shape of the curves remained constant indicating that neither further net acidity removal nor net oxidation were occurring.

In the cold room, the titration curve shapes remained essentially the same from 112 h to 15.5 days following set-up (Fig. 5g). There was no indication from the curves that Fe^{2+} oxidation had commenced. In the presence of a sediment, some acidity removal continued as indicated by the displacement of the curve to the left at pH 8.3 (Fig. 5h).

ICAP Analyses **of** Aeration Jar Samples: Samples from the aeration jars were collected 27 days after setup and sent for analysis by ICAP. Concentrations of the major components together with pH, Eh, conductivity and acidity for the same samples are summarised in Table 1. For the 'water only' samples, both filtered (0.45 µm pore size cellulose acetate filters) and unfiltered 'whole' samples were analyzed in order to determine whether metals are present in suspended solids. This is important since such material represents a precipitated yet potentially mobile source of contaminants. For the jars with sediments, filtered samples only were analyzed since it was not possible to collect water samples without inclusion of some sediment material.

The GD trap water is from an area where groundwater is entering Mud Lake and can reasonably be assumed to represent the most contaminated water which would require treatment. The GD trap water was characterised by a pH of 5.68, an Eh of +321 mV, a conductivity of 3290 µmho.cm^{-1} and an acidity of 2255 mg.L^{-1}. Both filtered and non-filtered samples were analysed by ICAP. Greater concentrations in the latter indicate the presence of contaminants within the suspended solid fraction. The dominant contaminants are Fe (1140 mg.L^{-1} in whole, 1010 mg.L^{-1} in filtered sample), *S* (1110 mg.L^{-1} in both whole and filtered samples) and Zn (85.7 mg.L^{-1} in whole and 81.3 mg.L^{-1} in filtered sample). The greater concentration of Fe and Zn in the whole, unfiltered sample indicates the presence of suspended solids which may include $Fe(OH)_3$ with coprecipitated metals as the sample appeared cloudy and orange.

The Jar 1 sample (GD trap water only, room temperature) after 27 days of aeration had little suspended solids as indicated by the very similar composition of the filtered and whole samples. As compared to the GD trap water, the Zn concentration was higher, (214-225 mg.L^{-1}) indicating that the GD trap sample was not representative of that added to the jars. The much lower Fe content of the Jar 1 water (239 mg.L^{-1}) compared to the GD trap water (1010 mg.L^{-1}) is in part attributable to settling of suspended $Fe(OH)_3$ present at set up and also the oxidation, hydrolysis and precipitation of Fe^{3+} as $Fe(OH)_3$ during the course of aeration. The ICAP data for Fe may be used to give a minimum rate

of Fe2+ oxidation in room conditions. If it is assumed that the oxidation process commenced at 88 h and reached equilibrium by 213 h (from titration curves), a rate of 103 $mg.m^{-3}.min^{-1}$ is obtained.

In Jar 4, (GD trap water, GD trap sediment, room temperature), pH and Eh values were similar to those in Jar 1 indicating that given sufficient aeration, oxidation is not inhibited by the presence of a sediment. Conductivity was a little lower, 3667 $\mu mho.cm^{-1}$ compared to 3832 $\mu mho.cm^{-1}$ for Jar 1, indicating that removal of some dissolved components may have been enhanced by the presence of a sediment. Iron concentration (138 $mg.L^{-1}$) was lower in the presence of a sediment (cf 239 $mg.L^{-1}$ in filtered sample from Jar 1), indicating that the sediment enhances Fe removal perhaps due to provision of more organic surface area favourable for adsorption processes. Acidity was substantially lower in the presence of a sediment, indicative of both the buffering capacity and also the enhanced removal of factors contributing to acidity (Fe^{3+}, Fe^{2+} and H^{+}). The high concentration of Al in Jar 4 (19.8 $mg.L^{-1}$) is attributable to release from the sediment associated with the drop in pH.

In Jar *6* (cold room, GD trap water only), the water chemistry of filtered and whole samples was similar indicating an absence of suspended solids. In the following discussion, only the numbers for the filtered sample will be given. In cold room conditions, oxidation rate was very slow as indicated above. The concentration of Fe (944 $mg.L^{-1}$) was similar to that of the GD water. Despite continuous aeration there was no evidence of significant oxidation either from the titration curves or the ICAP data. As at room temperature, Fe and acidity concentrations were much 50 % lower in the presence of a sediment (Jar 10) indicating the importance of sediment surfaces for Fe adsorption and both Fe^{2+} and H^{+} removal through ion exchange processes when oxidation is not occurring. Also as at room temperature, Al concentration was elevated in the presence of a sediment. The effect was much less dramatic however probably due to a higher pH (4.02) in the cold room.

2.3 Summary of Aeration Experiment

- At room temperature and with near saturation of dissolved oxygen, oxidation of Mud Lake, (GD trap) water commenced within 88 to 112 h as indicated by a lowering of pH below 3, increase in Eh beyond 500 mV and the appearance of an Fe^{3+} plateau in the NaOH titration curves.
- At a temperature of 2-5 °C (cold room), there was no indication of Fe^{2+} oxidation in the 376 h observation period. Eh and pH values remained more or less constant and titration curves maintained the same shape
- The presence of a sediment was associated with a removal of approximately 50 % of the acidity from the water. The titration curves and ICAP data indicate that much of this was due to removal of Fe^{2+} by sediments. The extent of acidity removal was similar at 20 °C and 2-5 °C.
- From 213 h to 376 h following set up, there was no net Fe^{2+} oxidation, indicating that an equilibrium state between Fe^{2+} oxidation and Fe^{3+} reduction had been attained.
- In the 88 h to 213 h period, the estimated oxidation rate at room temperature was 103 $mg.m^{-3}.min^{-1}$.
- The ICAP data indicate that little Zn removal occurred in association with aeration.

3.0 ARUM JAR EXPERIMENT

3.1 Methodology

2-L jars were set up with 850 mL of sediment. Mud Lake (GD trap) water was added until the total volume of water + sediment was 1.7 L. Prior to the test, the jars were kept in the cold room. Amendments were added to jars as shown in Table 2.

3.2 Results

Measurements of Eh, pH conductivity and temperature made 1-2 h after addition of amendments are shown in Table 2 and Figures 6a-f to 8a-f. The values were similar in all jars with pH in the range 4.2-4.8, Eh 404-437 mV and conductivity 3040 to 3327 $\mu mho.cm^{-1}$. Within 24 h of addition of amendments (Table 2), notable changes had occurred at room temperature. In the presence of potato waste added to the surface, pH declined to 3.5-4, ans some dissolution (cloudiness observed) and hydrolysis processes (as indicated by presence of gas bubbles associated with potato particles) occurred. Microbial mediated generation of volatile fatty acids through fermentation may have commenced but there was no noticeable VFA aroma for 3 or 4 days. In the presence of alfalfa, pH showed little change in the 24 h following set-up. Eh had declined somewhat in the presence of both types of amendment within 24 h of set-up. A further set of Eh readings was taken 48 h after set-up (Table 2). Further declines were observed in the amended room temperature jars. Values around -200 mV were found in some jars, almost low enough for sulphate reduction. Cold-room jars amended with alfalfa showed a small decline in Eh by 48 h after set-up.

Samples from some of the ARUM jars were collected 12 days after set-up and titrated with NaOH as for the oxidation test. Curves are presented in Fig. 9. Curves of all cold room samples were similar and showed the same shape as observed in the oxidation test. Clearly, there was little change in water chemistry in this period. At room temperature and in the absence of amendment, substantial Fe^{2+} oxidation had occurred as indicated by long Fe^{2+} (pH 5.5-7) and Fe^{3+} (pH 3.5) plateaux. In the presence of potato waste, oxidation had occurred (plateau at pH 3-4)and the pH 5.5-7 plateau was longer than in the unamended control, due either to reduction and dissolution of Fe(III) hydroxides present and/or production of VFAs through fermentation of the potato waste. In the presence of alfalfa in contrast, there was no indication that Fe^{2+} oxidation had occurred (pH remained above 4).

18 Days After Set-up: At 18 days after set-up, the jars were sampled again. The data (Table 2 and Figures 6a-f to **8a-9** show that dramatic changes have occurred in the room temperature jars. For the unamended jars (Jars 13-15), mean pH had dropped to 2.62, Eh had risen to 643 and conductivity remained close to the original value at 3428 µhmo.cm^{-1}. This indicates that considerable oxidation has occurred and that there has been little no net removal of dissolved species in the water column. This is confirmed in the titration curve. As observed in the oxidation experiment, some iron remains in the reduced, Fe^{2+} form. In the presence of alfalfa (Jars 1-6), pH had risen from the original values to a mean of 5.53 with 10 g per jar and 5.64 with 5 g per jar. Eh values remained low but well above those after 48 h. This is because the early wave of oxygen consumption and rapid hydrolysis and decomposition is over. However, the Eh values remained low at +57 mV with 10 g per jar and +96 mV with 5 g per jar. There was no evidence, either from the chemistry or appearance of orange precipitates, that Fe oxidation had occurred. Conductivity in jars with 10 g per jar alfalfa (Jars 1-3) was higher than initially (mean of 3711 µhmo.cm^{-1}). With *5* g of alfalfa, conductivity values (3163 µmho.cm^{-1}) were much below those of 24 h and a little below initial values suggesting removal of dissolved components. Mixing in of the alfalfa into the sediment (Fig. 8a-f) resulted in a higher pH, lower Eh and lower conductivity than placement on the surface, indicating a stimulation of anaerobic, pH raising processes. The titration curves (Fig. 10) indicate that acidity was reduced in the presence of alfalfa (compared to the unamended control) and all Fe was in the Fe^{2+} form.

Potato waste (Jars 7-12) gave the same overall trends as alfalfa at the 18 day sampling but pH values were not as high, Eh values not as low, and conductivity values were similar to those observed at 24 h. This indicates that ARUM activity was less well developed than with alfalfa.

The chemistry of amended jars in the cold room (Jars 22-33) was little changed from that at 24 h (Table 1, Fig. 7). In the unamended jars (Jars 34-36), the pH was a little reduced (mean of 3.53) and the Eh a little elevated (mean of 527 mV) from the previous

readings. This indicates that oxidation had commenced. However the titration curve for Jar 34 indicates all dissolved Fe in the Fe^{2+} or reduced form (Fig. 10) and there was no visible $Fe(OH)_3$, suggesting that oxidation was just commencing or occurring at a very low rate.

23 Days After Set-up-Titration Curves and ICAP Analyses: On day 23, 200 mL samples were taken from both room temperature and cold room jars with no amendment (Jars 13 and 34), 5 g alfalfa (Jars 5 and 26) and 2.5 g potato waste. The lower amendment concentrations were chosen since ARUM was as effective (increase in pH, decrease in Eh) as with the higher amendment rate and the lowest possible rate will be applied in the field. One hundred millilitres of each sample was filtered (0.45 µm pore, cellulose acetate filters). The differences in chemistry between the two'fractions give an indication as to whether there are significant, contaminant-bearing suspended solids. The filtered and unfiltered (whole) samples of these and the GD trap water added to the jars were submitted to an Assayer's laboratory for ICAP analysis. The results of analysis together with the chemistry of the unfiltered samples at time of sampling is summarised in Table 3a.

The GD trap water was characterised by high concentrations of Fe and S, both in excess of 1000 $mg.L^{-1}$. Zinc, the other contaminant of concern had a concentration of 81.3 $mg.L^{-1}$ and 85.7 $mg.L^{-1}$ in the filtered and whole samples respectively. Overall, there was little difference between whole and filtered samples indicating that the concentrations of suspended solids were low. In the samples from the unamended 'room-temperature' jar (Jar 13), Fe concentration (256-266 $mg.L^{-1}$) was approximately 75 % less than in the GD trap water. Much Fe has been removed through oxidation, hydrolysis and precipitation and/or complexation to organic matter. Aluminum at a concentration >7 $mg.L^{-1}$ was present whereas in GD trap water, concentrations were below the detection limit (0.025 $mg.L^{-1}$). With the drop in pH from 5.7 to 2.6, aluminum present within the sediments has been released into the water column. Zinc concentration (70-75 $mg.L^{-1}$ was a little lower than in GD trap water, perhaps due to coprecipitation with $Fe(OH)_3$ or

complexation to organic surfaces,

The chemistry of water from Jar 5, amended with 5 g of alfalfa, was very different from both the original GD trap water and from that of the unamended jar. The pH (6.26) was substantially higher than the GD trap water (pH 5.68) and the unamended jar (pH 2.57). Eh (+61 mV) was much lower and conductivity lower than in those two samples, indicating more reducing conditions and consequent removal of more dissolved species. Iron concentrations were much lower than in the GD trap water but higher than in the unamended Jar 13. The titration curve (Fig. 11) indicates that all of the Fe is present as Fe^{2+} favoured by the high pH conditions. Some of the iron may be due to reductive dissolution from the sediments. Sulphur concentrations were 25-30 % lower than in GD trap water and less than in the unamended samples (Jar 13) indicating that sulphate reduction and metal sulphide precipitation may have taken place. Eh values measured in the water column were never sufficiently low (<-220 mV) for sulphate reduction but such conditions may have been present within the sediment. Zinc concentration was reduced to 13.2 $mg.L^{-1}$ in the non-filtered sample and to 0.025 $mg.L^{-1}$ in the filtered sample. The difference between the filtered and unfiltered samples is very interesting and indicates the association of some Zn with suspended solids, probably organic colloids. It should be noted that at this time, the water column was black from visible suspended particles. Other elements including P and Al were also greater in the unfiltered sample indicating that they too are associated with suspended materials. Although Zn is present in the unfiltered sample it should be pointed out that the concentration (13.2 $mg.L^{-1}$) is very much lower than in either the unamended jar samples or the GD trap water.

The sample from the potato amended Jar 11 was characterised by a very low Eh value (-211 mV), almost low enough to support sulphate reduction. Its conductivity was lower (2747 $\mu mho.cm^{-1}$) and pH higher (5.86) than the unamended jar sample or the GD trap water. Iron concentrations were lower than in GD trap water but higher than in either the alfalfa or unamended jars. Conditions were favourable for bacterially mediated iron

reduction (low Eh) and the titration curve (Fig.11) indicates that nearly all of the dissolved Fe was in the Fe^{2+} form. It should be noted that at this time (23 days after set up), the acidity of this Jar was much lower than at 18 days although still a little higher than in the unamended jar due no doubt to the presence of VFAs from the decomposition of the potato waste. Almost all the Zn had been removed from the water column of this potato amended jar. In other words, in contrast to the alfalfa jar (Jar 5), there was little Zn in the unfiltered sample i.e. there was no or little Zn associated with suspended particles.

In samples from the cold room jars, changes in the chemistry were much less dramatic than at room temperature as a consequence no doubt of reduction in chemical and more particularly microbially mediated reaction rates at the lower temperature.

54 Days After Set-up: Data on pH, Eh and conductivity for all the jars were collected **54** days after set-up in particular to determine whether ARUM was active in cold room conditions.

At room temperature, the trends noted at 18 and 23 days after set up continued (Fig. 6a-f to 8a-9. In unamended jars (Jars 13-15), pH remained around 2.6. This together with data from the oxidation experiment indicates that this is about the lowest pH that might be expected in Mud Lake. Eh in unamended jars rose further to a mean of +730 mV. Conductivity remained near original values indicating as before, no net removal of dissolved species in these conditions. In contrast, in amended jars, pH continued to climb to higher than 7 with the higher amendment rate of both alfalfa and potato waste. Eh values had generally declined further, indicating reducing condition remain, favourable for ARUM processes. The most striking change from the 18 day data was the steep decline in conductivity. The greatest change was with potato waste at 5 g per jar where conductivity had declined to 1685 $\mu hmo.cm^{-1}$, approximately 50 % of the original values. ARUM was actively removing dissolved ionic species from the water column. At this time, there were no clear differences between jars with surface

amendment or with the amendment mixed in.

By day 54, substantial changes in the water chemistry of the cold room jars were evident. In alfalfa-amended jars, pH had risen to values above 6 and with potato, above than **5,** higher than observed for the room temperature jars at 18 days. All the amended cold room jars (Jars 22-33) gave off an aroma of VFAs, gas bubbles were rising from the sediments and the water column was cloudy, all indications of microbial activity. Eh values were much lower than initially. Conductivities were similar to initial values but lower than observed at 18 days indicating that contaminant removal processes had likely commenced. In the absence of amendments (Jars 34-36), pH had declined to a mean of 3.42 and Eh had risen to +604 mV. Although no orange $Fe(OH)_3$ precipitates had formed, these measurements indicate that Fe^{2+} oxidation had commenced.

72 Days After Set-up: At 72 days from set up, some of the ARUM jars were sampled. The data for pH, Eh and conductivity are summarized in Table 2. In room temperature conditions, pH values were similar to those on day 23. Eh values remained low in the presence of amnedments although a little higher than on day 23. Conductivity continued to decline in these amended jars indicating that the sediment is acting as a net sink for dissolved components in the water column. Values were approximately 40 % lower than at the start of the experiment. The acidity tiration curves (Fig. 12) indicate that in the presence of amendments (Jar 5-alfalfa, and Jar 1I-potato waste) nearly all the acidity had been removed. In the unamended jar (Jar 13), Fe was present in both Fe^{2+} and Fe^{3+} forms indicating that an equilibrium remains as was found in the oxidation experiment. The plateau at pH *5* is probably due to Al. The H_2SO_4 titrations (Fig. 13) indicate little alkalinity present in the potato waste jar (Jar 11) but substantial alkalinity present in the alfalfa jar (Jar *5).* The shape of the curve (precipitous drop at pH *5.5)* indicates that bicarbonate is probably responsible for much of this alkalinity).

In the cold room, and in the presence of amendments, pH remained around 6. Eh showed a further decline from day 23 in these jars. Conductivity also declined indicating

removal of dissolved components to the sediment. The acidity titration curves (Fig. 12) indicate that Fe remains in the reduced form. In jar 34 (no amendment), pH had declined to below 3. This and the titration curve (Fig. 12) clearly indicates that oxidation had commenced in the absence of organic amendements. Two samples, from Jar 32 (cold room, 2.5 g potato waste) and Jar 34 (cold room, no amendment) were submitted for ICAP analysis to determine whether oxidation and ARUM had altered the water chemistry in these jars.

The data are summarized in Table 3b. In the potato waste amended jar, there was very little Zn (0.334 $mg.L^{-1}$) remaining in the water. ARUM had effectively removed Zn from the water column between day 23 and day 72. The water still contained substantial quantities of S (620 $mg.L^{-1}$) but the concentration was lower than at day 23 (750 $mg.L^{-1}$). Interestingly there was substantial Fe (546 mg.L-1) remaining in the water column. In contrast, in Jar 34, with no amendment, substantial oxidation had occurred. Zn concentrations remained high (124 $mg.L^{-1}$). Iron concentration (129 $mg.L^{-1}$) was much reduced from day 23 (700 $mg.L^{-1}$) indicating the hydrolysis and precipitation of Fe^{3+} as $Fe(OH)_3$.

Field Samples of February 26, 1995: Five samples collected in the field on February 26, 1995 were analysed by ICAP. These indicate the variety of water chemistries present in Mud Lake near the end of the period of ice cover. Titration curves for these and other locations are shown in Fig. 14a-c and indicate that all the Fe is in the reduced Fe^{2+} form. Under the ice, conditions are unfavourable for oxidation as was found with the cold room jars. This indicates that even if temperatures are too low for substantial microbial activity, there will likely be no oxidation of groundwater entering Mud Lake before it leaves the lake.

3.3 Summary of ARUM Experiment

- At room temperature, jars with added alfalfa or potato waste were active in ARUM (removal of metals associated with alkalinity generating anaerobic microbial processes).
- In the absence of amendments, the GD trap water added to jars was actively oxidising by this time.
- By day 23, in the presence of amendments, virtually all the dissolved Zn had been removed from the water column
- With alfalfa, but not with potato, a portion of the removed dissolved Zn was associated with suspended solids
- By day 54, at room temperature, up to 50 % of the total dissolved ions had been removed in the presence of amendments whereas without amendments, conductivity remained constant
- In the cold room (1-5 ° C), ARUM activity had commenced by day **54,** and in the presence of potato waste, had removed nearly all the dissolved Zn by day 72, indicating that even in winter conditions, ARUM can operate in Mud Lake

From this study, it can be concluded that ARUM can effectively remove Zn and acidity from groundwater entering Mud Lake but that it is essential to add organic amendments for this to occur. Both amendments tested, alfalfa and potato waste, effectively removed Zn and acidity, but the potato waste is the preferred option since with alfalfa, some of the Zn removed from the dissolved fraction was associated with suspended solids. This is undesirable since such material is potentially mobile and may carry Zn out of Mud Lake.

4.0 **Overall** Summary

The data for the aeration and ARUM tests are summarised together in Table 4. It is clear that in the absence of added decomposable organic amendments, oxidation will proceed in summer (room temperature conditions). By 213 h, and for the samples shown in the table (oxex Jarl, oxes Jar4 and Jar 13), an equilibrium state exists with large pools of both Fe^{2+} and Fe^{3+}. The data do not allow a determination of Fe cycling rates, i.e. it is not clear whether the Fe^{2+}/Fe^{3+} is associated with an active oxidation/precipitation/reduction /dissolution cycle. The presence of a sediment accounts for removal of a substantial proportion of dissolved iron, with or without aeration. The presence of decomposable organic material (potato waste) gives rise to reducing conditions and almost total removal of Zn from the water column.

In cold room conditions, as may be expected to occur in winter under the ice, there was no measurable oxidation over a 27 day period. It is likely that in the field, most Fe will remain in the Fe^{2+} state as was found for the GD trap sample collected in December. ARUM can proceed at low temperatures and may allow for removal of Zn from the water column under the winter ice.

5.0 **Design Criteria for Scale-up in the Field**

Data from the aeration test, which removed iron, and the ARUM experiment, which effectively removed Zn, can be used to derive removal rates per unit volume of water, per unit area of sediment and per unit weight of organic amendment. In turn, these rates can be used to design field-treatment systems for the groundwater entering Mud Lake. Requirements for the field are based on groundwater entering Mud Lake at a rate of 1 L.sec-1. This is preferred to figures based on total flux of water to and from Mud Lake as the figure would change dramatically after construction of a diversion ditch.

5.1 Iron Removal rates in the Aeration Test

Oxidation and the subsequent precipitation of the GD trap water was slow. The first signs of oxidation (drop in pH to <3) were evident in titration curves of the room temperature samples (with or without sediment) after some 65 h of aeration. Complete oxidation was never achieved and an equilibrium between Fe^{2+} and Fe^{3+} was achieved at around 165 to 213 h with a substantial amount of Fe remaining in the reduced, Fe^{2+}, form.

The difference in Fe content of the water added to the jars and after 27 days of aeration can be used to estimate rates of Fe removal through Fe^{2+} oxidation, hydrolysis and precipitation as $Fe(OH)_3$. Such estimates for OXEX Jar 4, containing GD trap water and sediment and kept at room temperature (19-23°C) are shown in Table 5a . This jar represents the most realistic model for what may happen in the field with much wind-driven mixing and consequent high O_2 concentration in the water column. A removal rate of 1.98 $mg.m^{-2}.min^{-1}$ was estimated. From this and the estimated groundwater entering Mud Lake (assumed to have an Fe concentration equal to that of the GD trap water), the area required to 'treat' the water as occurred in Jar 4 may be estimated. The result is 35.3 ha, four times the area of the lake, indicating that oxidation and precipitation to the extent observed in OXEX Jar 4 (1002 mg/L) removed could not be achieved in the field. Since in cold room conditions, oxidation and precipitation are very much slower, the field oxidation would be slower than the estimate based on OXEX Jar 4.

5.2 Zn Removal Rates in the ARUM Experiment

The laboratory experiment demonstrated that at room temperature, and in the presence of reducing conditions induced by addition of decomposable, organic amendments, Zn was effectively removed from groundwater which had entered Mud Lake (GD trap water) in a period of 23 days. In cold room conditions (1-5oC), Zn removal was completed

within 72 days in the presence of potato waste. From the lab experiment, Zn removal rates can be estimated both in terms of area of sediment and volume of water. The estimates are summarised in Table 5b . Removal rate of 0.18 $mg.m^{-2}min^{-1}$ was estimated based on data for Jar 11 which had been amended with 2.5 g of potato waste. With this rate, it can be estimated that in order to treat the annual estimate groundwater inflow of 1 $L.sec^{-1}$, an area of 4838 m^2 and addition of potato waste (442 $g.m^{-2}$) once a year would be required. Alternatively an area of 1613 m^2 with 3 additions of potato waste (442 $g.m^{-2}$) per year. The water would need to be exposed to reducing conditions for at least 23 days. The cold room data and the February 1995, field sample data, indicate that reducing conditions can be established and maintained under the winter ice cover on Mud Lake.

5.3 Design **for** Scale-up

Since ARUM worked effectively on groundwater entering Mud Lake with Fe in the reduced form, it is not necessary to preoxidize the water for Fe removal prior to ARUM. It makes sense to treat the water in the vicinity of entry ('black holes'). Some of if not most of the Fe will be removed by ARUM. Iron remaining in the water could subsequently be removed by exposure to oxidising conditions before leaving Mud Lake. An enclosure within Mud Lake with a single effluent location would allow for manipulation of retention time and monitoring of effluent quality. Such an enclosure would optimise control of exposure of groundwater to ARUM conditions.

From the above, an area of 1612 m^2 or approximately 40 x 40 m would be a sufficient area for the sediment-bound ARUM processes to remove the annual loading of Zn in groundwater entering Mud Lake. Such an area would require 3 annual additions of potato waste which could be following ice break up, in mid-summer and before freeze-over in the fall. Much of this groundwater is believed to enter in the 'black-hole' areas in a small part of the lake. A single enclosure or several smaller enclosures could be

constructed around the black-hole areas to treat most of this water. An effective retention time of at least 23 days would be required in summer conditions. Estimates of groundwater inflow rates would be measured in the field prior to final design and construction. An enclosure could be constructed of Fabrene material anchored into the sediment. This technology has been successfully implemented elsewhere. The enclosure will be designed such that water leaves at one location where it can be sampled to determine the effectiveness of the ARUM process. Data from influent and effluent water will be mobitored regularly and if necessary, modifications to the system made to improve water treatment effectiveness.

Water leaving the enclosures would be exposed to oxidising conditions outside the enclosure and if Fe remains in solution, much will be removed through oxidation, hydrolysis and precipitation of $Fe(OH)_3$ prior to leaving Mud Lake.

The exact location and dimensions of the ARUM enclosure(s) would be determined in the field after ice break up.

Table 1: Mud Lake oxidation experiment - Chemistry 27 days after set up

Parameter (mg/L)	Det.lim. (mg/L)	OXEX J1 Room temp No sedt. Whole	OXEX J1 Room temp No sedt. Filtered	OXEX J4 Room temp Sedt. Filtered	OXEX J6 Cold room No sedt. Whole	OXEX J6 Cold room No sedt. Filtered	OXEX J10 Cold room Sedt. Filtered	ML 18 Whole	ML 18 Filtered	GD Trap Whole	GD Trap Filtered
pH		2.44		2.48	3.96		4.02			5.68	
Eh (mV)		718		760	449		445			321	
Conductivity (umho/cm)		3832		3667	3548		2954			3290	
Acidity (mg/L equiv.CaCO3)		1871		1065	1866		1129	230		2255	
Al	0.025	0.557	0.591	19.8	0.116	0.216	4.39	0.166	0.161	<	<
Co	0.005	0.457	0.44	0.947	0.423	0.423	1.03	0.042	0.041	0.438	0.412
Fe	0.005	248	239	138	963	944	446	64	58.3	1140	1010
P	0.06	<	<	<	<	<	<	0.28	0.11	<	<
K	0.4	15.8	17.1	16.1	11.4	13.5	14.1	7.3	7.2	16.9	15.9
Na	0.04	11	11.6	13.1	10.4	11.5	12	4.04	4.06	10.1	9.8
S	0.08	1040	974	1070	1070	1040	933	159	154	1110	1110
Zn	0.005	225	214	228	85.4	85.5	125	8.68	8.58	85.7	81.3

Table 2: Mud Lake ARUM Experiment - pH, Eh and Conductivity
Each value is mean of 3 jars

	Jars	Temperature regime	Amendment g/jar	pH	Eh mV	Conductivity umho/cm
GD trap water				5.68	321	3290
At set up	1-36	Room temp.		4.45	418	3222
After 1 day	1-3	Room temp.	alfalfa 10	4.74	299	3875
	4-6		alfalfa 5	4.41	360	3617
	7-9		potato 5	3.9	409	3617
	10-12		potato 2.5	3.86	422	3533
	13-15		none	3.6	474	3426
	16-18		alfalfa 10 mixed in	4.95	183	3663
	19-21		potato 5 mixed in	4.82	295	3386
	22-24	Cold room	alfalfa 10	4.76	340	3728
	25-27		alfalfa 5	4.71	338	3466
	28-30		potato 5	4.13	389	3359
	31-33		potato 2.5	4.17	396	3352
	34-36		none	4.17	438	3265
After 2 days	1-3	Room temp.	alfalfa 10		-188	
	4-6		alfalfa 5		-120	
	7-9		potato 5		170	
	10-12		potato 2.5		418	
	13-15		none		536	
	16-18		alfalfa 10 mixed in		104	
	19-21		potato 5 mixed in		-174	
	22-24	Cold room	alfalfa 10		326	
	25-27		alfalfa 5		337	
	28-30		potato 5		377	
	31-33		potato 2.5		395	
	34-36		none		433	
After 18 days	1-3	Room temp.	alfalfa 10	5.53	57	3711
	4-6		alfalfa 5	5.64	96	3163
	7-9		potato 5	4.69	219	3684
	10-12		potato 2.5	5.18	83	3474
	13-15		none	2.62	643	3428
	16-18		alfalfa 10 mixed in	6.14	-53	3270
	19-21		potato 5 mixed in	4.64	271	3671
	22-24	Cold room	alfalfa 10	4.2	428	3566
	25-27		alfalfa 5	4.09	451	3471
	28-30		potato 5	4.2	441	3553
	31-33		potato 2.5	4.09	458	3452
	34-36		none	3.53	527	3505
After 54 days	1-3	Room temp.	alfalfa 10	7.13	-96	2052
	4-6		alfalfa 5	6.16	32	2322
	7-9		potato 5	7.09	-21	1685
	10-12		potato 2.5	6.27	79	2389
	13-15		none	2.61	730	3288
	16-18		alfalfa 10 mixed in	6.95	0	1940
	19-21		potato 5 mixed in	6.33	89	2073
	22-24	Cold room	alfalfa 10	6.09	193	3565
	25-27		alfalfa 5	6.19	197	3334
	28-30		potato 5	5.22	270	3326
	31-33		potato 2.5	5.4	241	3302
	34-36		none	3.42	604	3256
After 72 days	5	Room temp.	alfalfa 5	6.85	145	1886
	11		potato 2.5	6.09	275	1787
	13		none	2.82	735	2840
	16		alfalfa 10 mixed in	6.88	73	1375
	26	Cold room	alfalfa 5	5.93	101	2856
	32		potato 2.5	5.78	168	2531
	34		none	2.98	626	3220

Table 3a: Mud Lake ARUM - chemistry of samples 23 days after set up

Parameter (mg/L)	Det.lim. (mg/L)	GD Trap		Jar 5 Room temp Alfalfa 5 g		Jar 11 Room temp Potato 2.5 g		Jar 13 Room temp No amendment
		Whole	Filtered	Whole	Filtered	Whole	Filtered	Whole
pH		5.68		6.26		5.86		2.57
Eh (mV)		317		61		-211		660
Conductivity (umho/cm)		3290		2997		2747		3259
Acidity (mg/L equiv.CaCO3)		2255		738		1235		1045
Al	0.025	<	<	0.531	0.195	0.071	0.202	7.39
Co	0.005	0.438	0.412	0.007	<	0.017	0.017	0.403
Fe	0.005	1140	1010	434	366	619	615	266
P	0.06	<	<	2.11	0.67	0.68	0.53	<
K	0.4	16.9	15.9	111	92.9	38.2	34.2	13.5
Na	0.04	10.1	9.8	20.8	13	20.8	18.4	11.9
S	0.08	1110	1110	712	649	741	755	892
Zn	0.005	85.7	81.3	13.2	0.025	0.625	0.214	74.6

Table 3b: Mud Lake ARUM; Field samples of February 25 and cold room samples 72 days after set up (filtered, acidified samples)

Parameter (mg/L)	Det.lim. (mg/L)	Jar 32 Potato 2.5	Jar 34 No amend	ML NE arm	ML A-6	ML B-1	ML B-6	ML C-5
pH		5.78	2.98	5.36	4.81	5.26	5.09	5.73
Eh (mV)		168	626	60	168	100	118	42
Conductivity (umho/cm)		2531	3220	522	375	836	722	1043
Acidity (mg/L equiv.CaCO3)		1302	857	179.6	127.2	252.8	240.3	268.6
Alkalinity (mg/L equiv.CaCO3)		216	-	42.9	0	17.7	7.1	45.4
Al	0.025	<	11.1	0.079	0.081	0.037	0.046	0.059
Co	0.005	<	0.473	0.021	<	0.029	0.011	0.04
Fe	0.005	546	129	50.2	35.3	57.8	72.1	83
P	0.06	0.06	<	<	<	<	<	<
K	0.4	23.7	11.9	3.7	4.5	5.9	4.3	4.8
Na	0.04	11.9	12.6	2.75	3.64	5.49	3.55	6.08
S	0.08	620	768	83.9	51.8	156	121	173
Zn	0.005	0.334	124	4.25	0.344	5.65	1.28	7.71

	Jar 26 Cold room Alfalfa 5 g		Jar 32 Cold room Potato 2.5 g		Jar 34 Cold room No amendment	
Filtered	Whole	Filtered	Whole	Filtered	Whole	Filtered
	4.29		4.41		3.68	
	446		438		535	
	3318		3167		3276	
	1619		1496		1530	
7.15	1.51	1.51	1.26	1.16	3.38	3.19
0.389	0.364	0.35	0.396	0.372	0.441	0.422
256	710	696	750	692	700	661
<	0.3	0.27	0.1	0.09	<	<
14	100	87.1	50.7	33.9	14.1	13.4
12.7	12.2	11.4	19.8	11.1	12.1	11.9
864	1010	997	968	896	1020	1020
71.7	61.3	58.3	68.2	64	101	96.1

ML600mN,7
5.87
78
82
41.3
31
0.109
<
1.75
<
2.1
1.78
1.67
0.122

Table 4: Summary of Oxidation and ARUM Experiments

	Field (December)		Room temperature				Cold Room			
Parameter	GD Trap	ML 18	OXEX J1	OXEX J4	Jar 13	Jar 11	OXEX J6	OXEX J1	Jar 34	Jar 32
Sediment			No	Yes	Yes	Yes	No	Yes	Yes	Yes
Aeration			Yes	Yes	No	No	Yes	Yes	No	No
Organic amendment			No	No	No	Yes	No	No	No	Yes
pH	5.68	2.91	2.44	2.48	2.57	5.86	3.96	4.02	3.68	4.41
Eh (mV)	321	628	718	760	660	-211	449	445	535	438
Conductivity (umho/cm)	3290		3832	3667	3259	2747	3548	2954	3276	3167
Acidity (mg/L equiv.CaCO3)	2255	230	1871	1065	1045	1235	1866	1129	1530	1496
Fe (mg/L)	1010	58	239	138	256	615	944	446	661	692

Readings for aerated jars (OXEX Jars) - 27 days after set up

Readings for non-aerated jars (Jar 13, Jar 34) - 23 days after set up

Fe concentrations are for filtered samples

Table 5a: Requirements for Fe removal in Mud Lake in oxidizing conditions
Based on laboratory aeration experiment

	If groundwater enters Mud Lake at 1 L/sec and [Fe] is 1140 mg/L (GD trap data)
35.95	tonnes per year of Fe is entering Mud Lake
	In laboratory aeration experiment at room temperature
1002	mg/L removed in 27 days in Jar 4 (room temperature, GD trap sediment)
113	cm2 surface area of sediment in Jar
0.85	L of GD trap water in Jar
1.94	mg/m2/min of Fe removed
21.91	mg/m3/min of Fe removal
1.02	kg removed per m2 per year
35,284	Area (m2) required to remove 1002 mg/L Zn

Table 5b: Potato waste and area required to treat Mud Lake with ARUM
Based on laboratory jar experiment and ICAP analysis for Zn

	113	surface area of jar (cm2)
	0.85	Vol of water in jar (mL)
	69.1	Zn content of water (mg) if concn is 81.3 mg/L)
	0.214	Zn conc. at day 23 (mg/L)
	68.9	Zn removed (mg/jr) in 72 days (cold room) or 23 days (room temperature)
1-5 C	20 C	
1.13	3.52	Removal rate in mg/L/day assuming constant removal rate
0.78	2.45	Removal rate in mg/m3/min
85	265	Removal rate in mg/m2/day
0.059	0.184	Removal rate in mg/m2/min
		At a rate of 221 g/m2 of potato waste, ARUM will remove 265 mg/m2 of Zn
		in a 23 day period in summer conditions or a 72 day period in winter
	1.20	Amount of Zn (tonnes) removed by 1 tonne of potato waste in this configuration
		ARUM requirements based on groundwater flow of 1 L/sec and [Zn] of 81.3 mg/L (GD trap sample)
	2.564	Total estimated Zn entering Mud Lake GD trap chemistry) in tonnes
	2.138	Potato waste required to remove Zn (tonne)
	9,675	Area (m2) to remove annual Zn loading at 221 g/m2of potato waste
	4,838	Area (m2) to remove annual Zn loading at 442 g/m2 of potato waste
	3,225	Area required (m2) if potato waste applied at 221 g/m2, 3 times per year
	1,613	Area required (m2) if potato waste applied at 442 g/m2, 3 times per year

221 g/m2 potato waste is equivalent to 2.5 g/jar
442 g/m2 potato waste is equivalent to 5 g/jar

Fig.1: Mud Lake oxidation experiment
pH

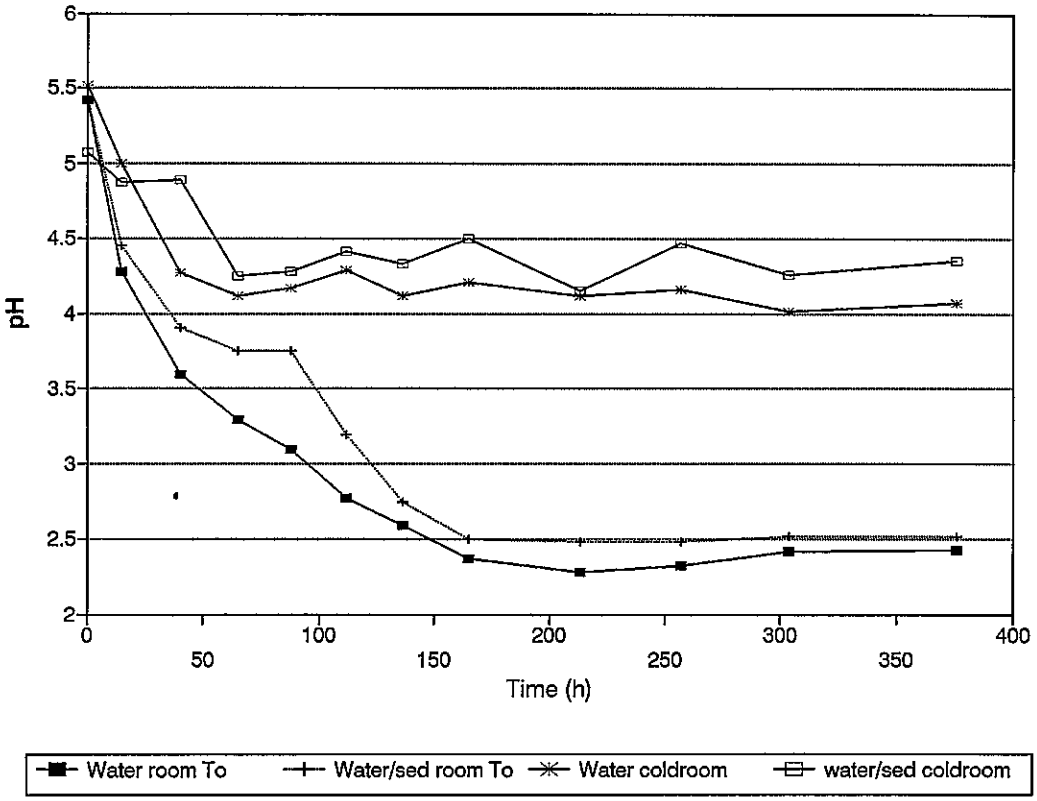


Fig.2: Mud Lake oxidation experiment
Eh

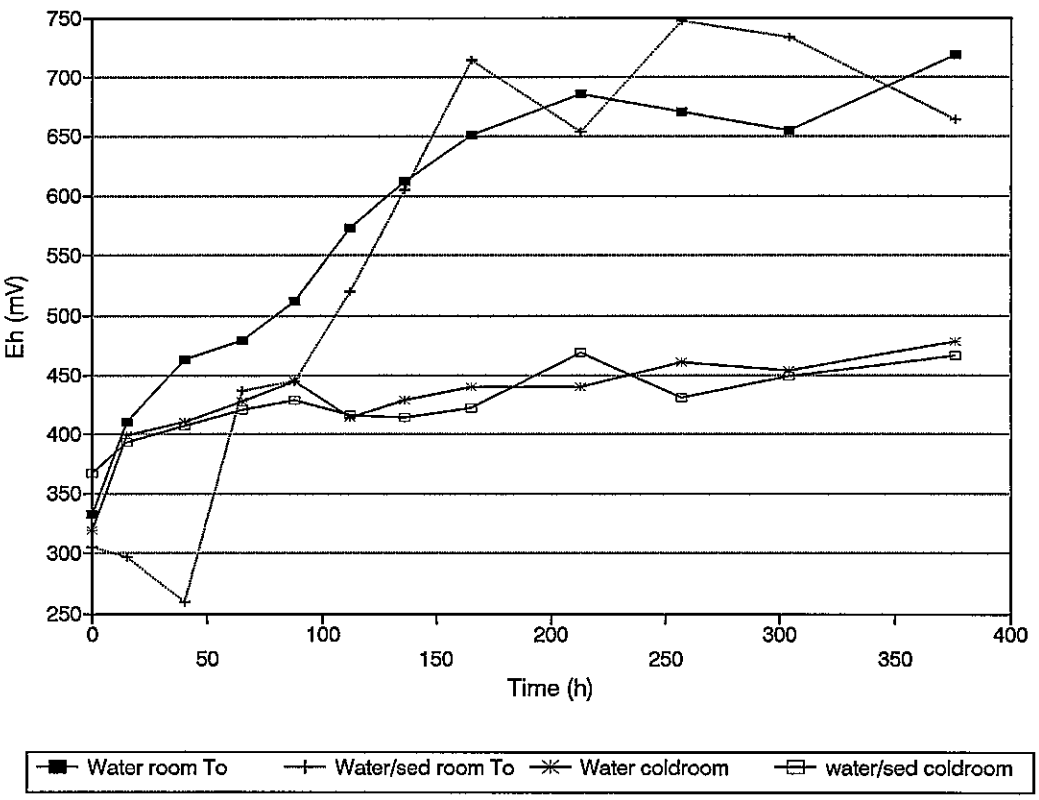


Fig.3: Mud Lake oxidation experiment
Conductivity

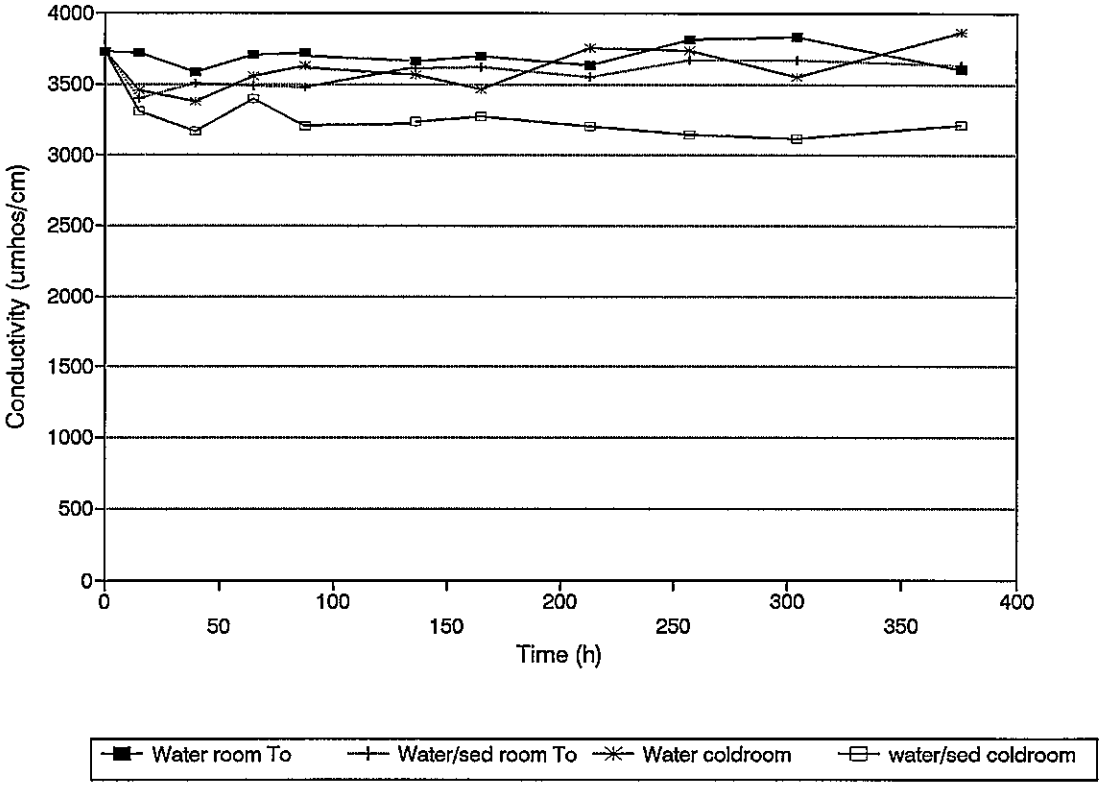


Fig. 4: Mud Lake oxidation experiment
Acidity

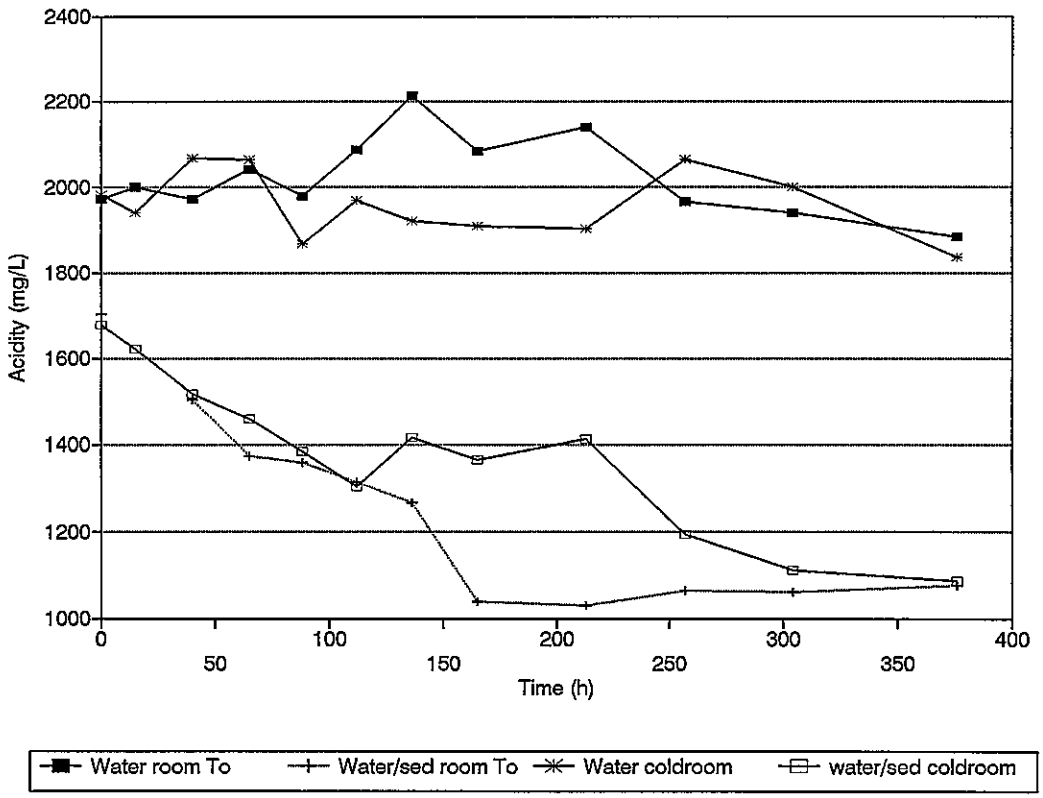


Fig. 5a: Mud Lake Oxidation
Jar 1 (room temp, no sediment)

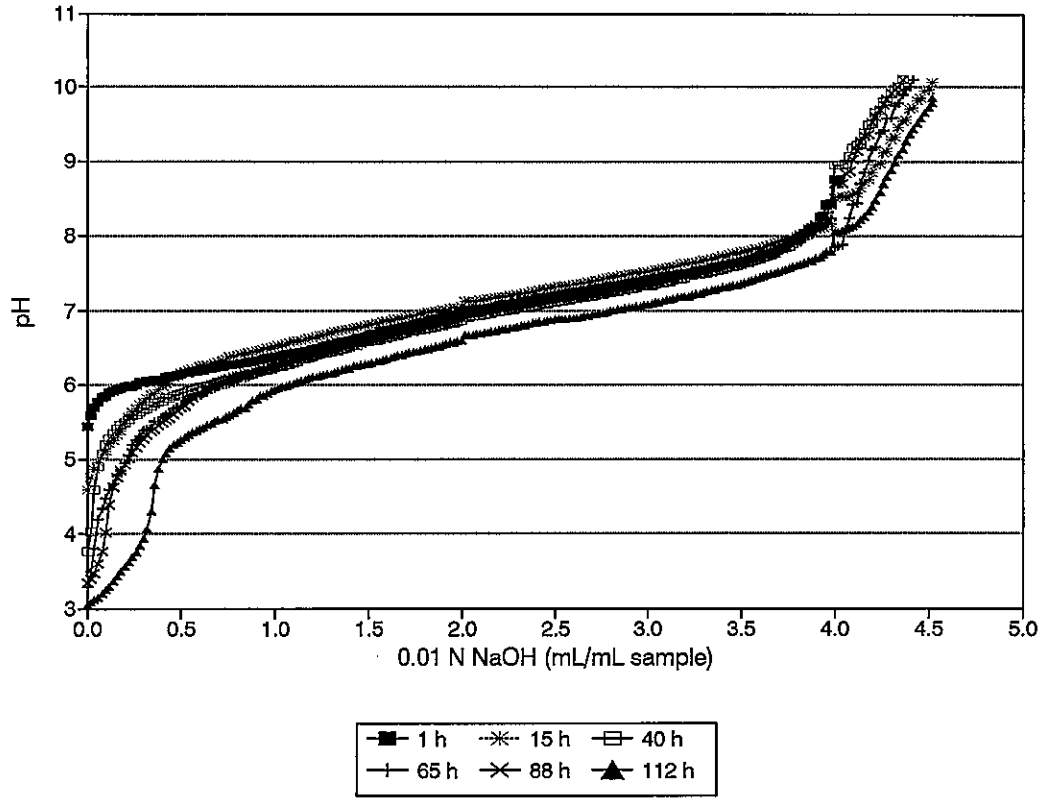


Fig. 5b: Mud Lake Oxidation
Jar 4 (room temp, sediment)

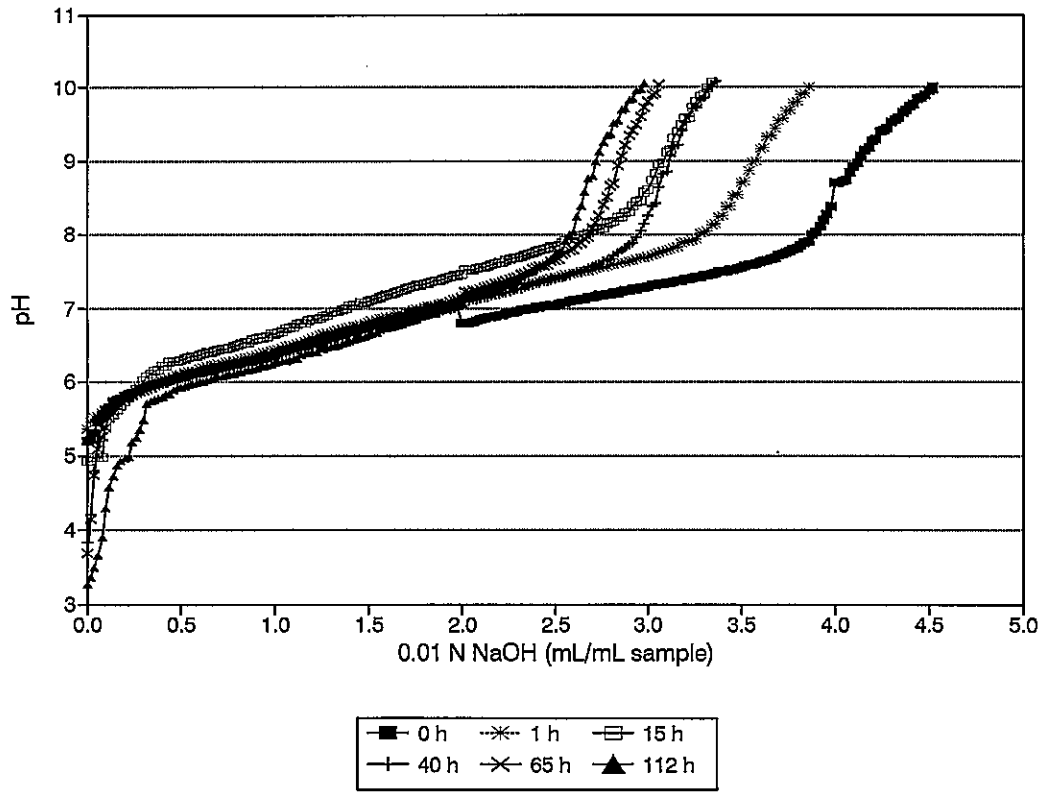


Fig. 5c: Mud Lake Oxidation
Jar 6 (cold room, no sediment)

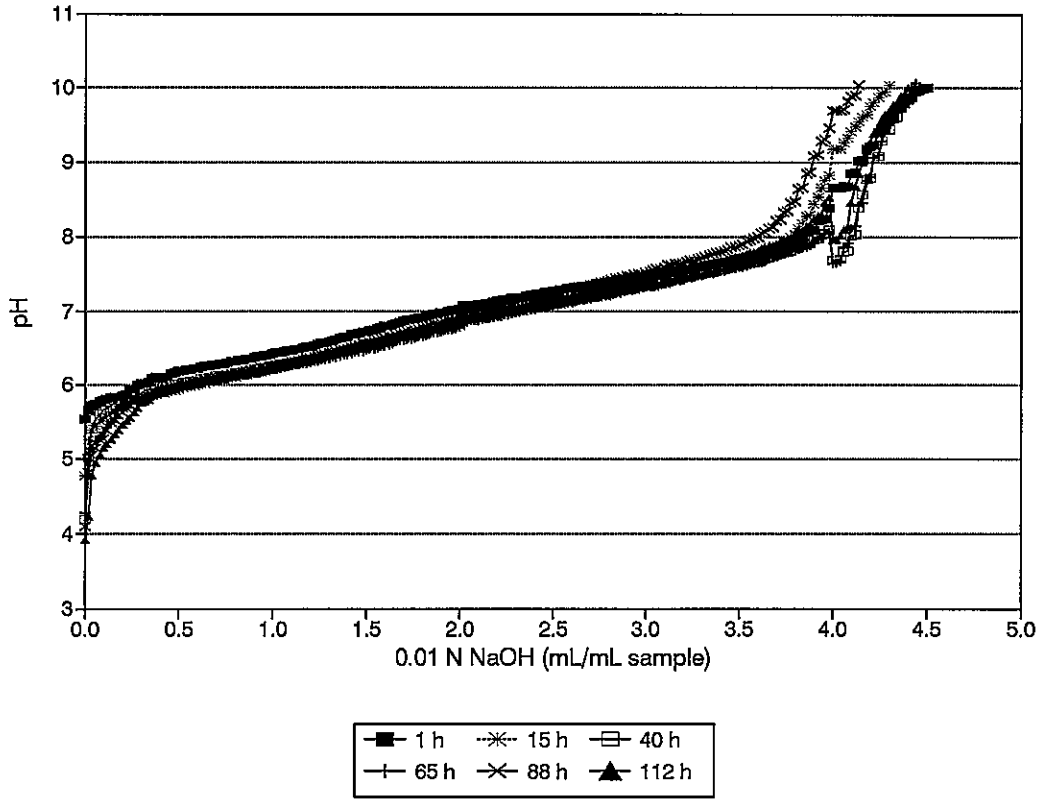


Fig. 5d: Mud Lake Oxidation
Jar 9 (cold room, sediment)

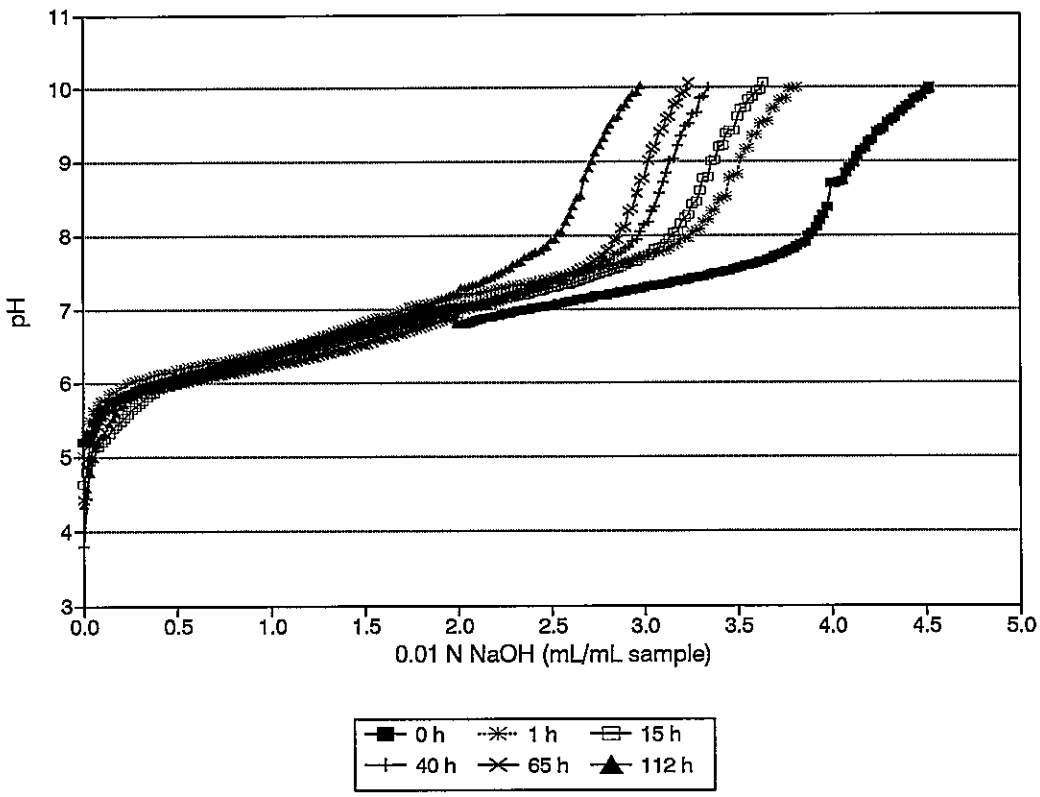


Fig. 5e: Mud Lake Oxidation (cont.)
Jar 1 (room temp, no sediment)

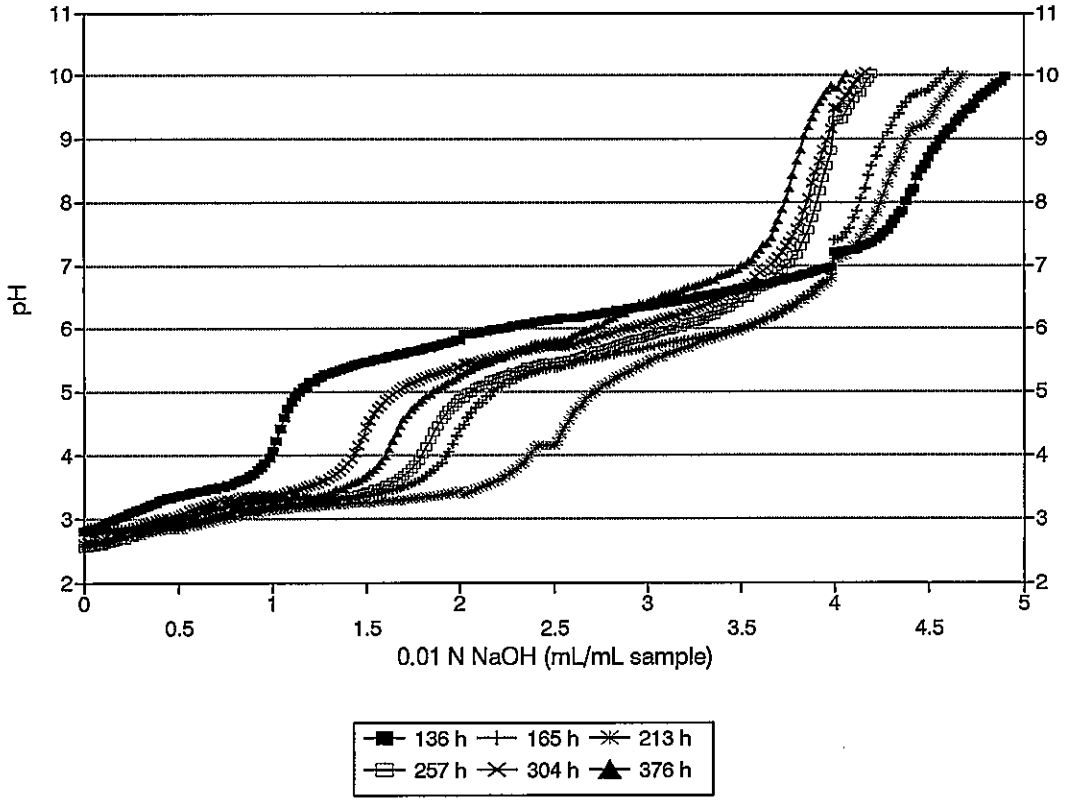


Fig. 5f: Mud Lake Oxidation (cont.)
Jar 4 (room temp, sediment)

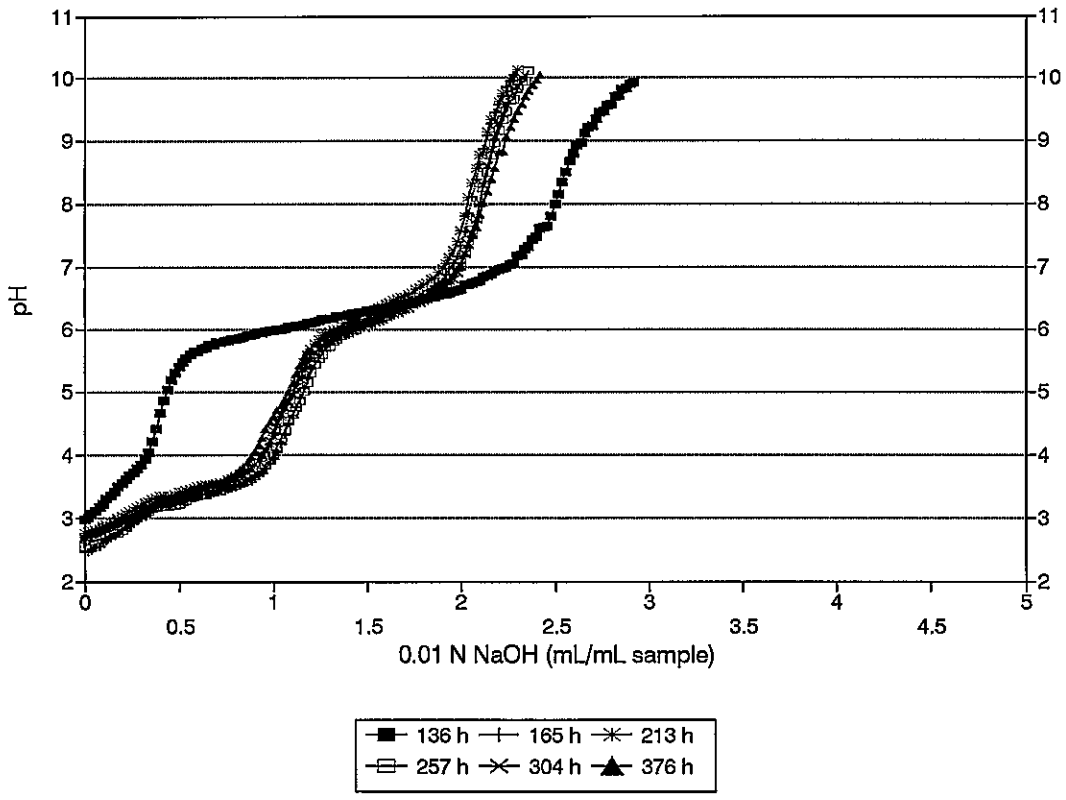


Fig. 5g: Mud Lake Oxidation (cont.)
Jar 6 (cold room, no sediment)

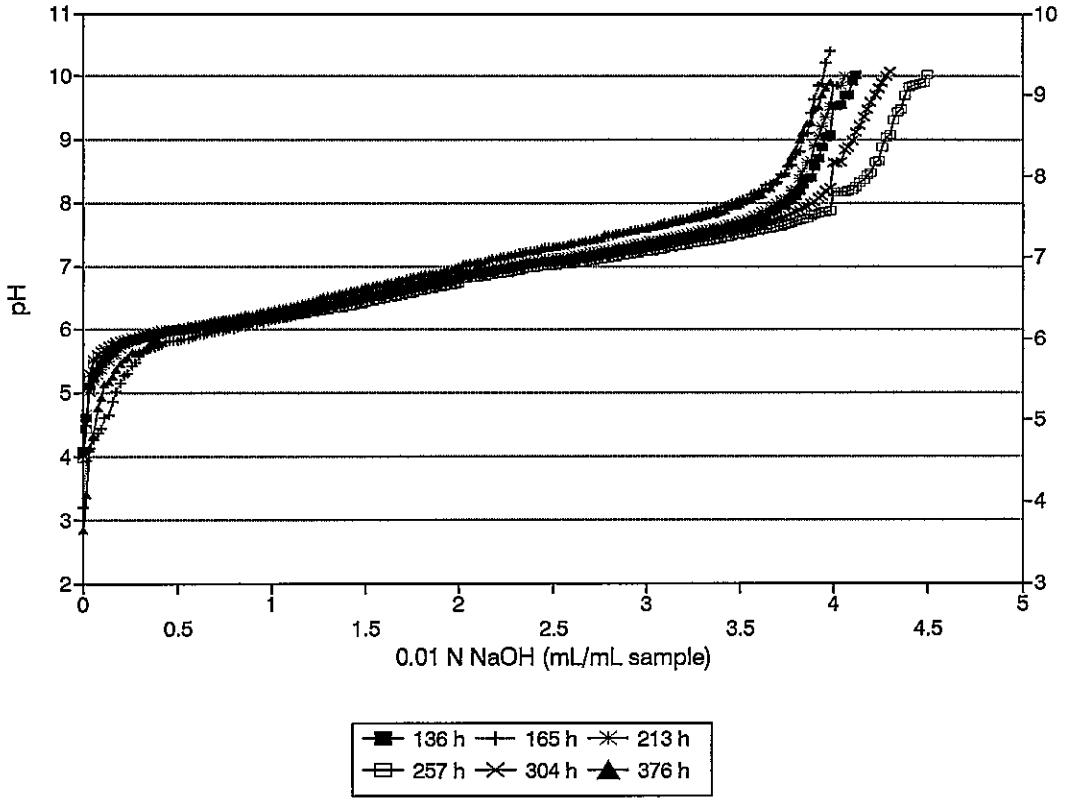


Fig. 5h: Mud Lake Oxidation (cont.)
Jar 9 (cold room, sediment)

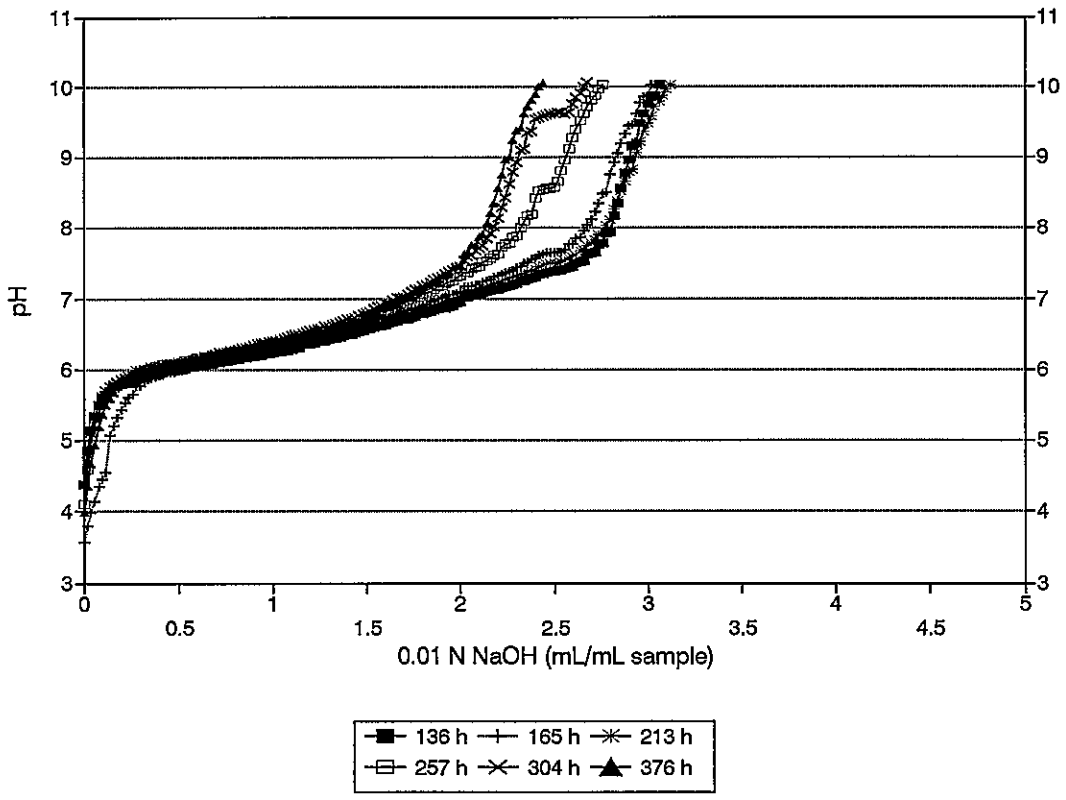


Fig. 6a: Mud Lake ARUM Experiment
Potato jars room temp, pH

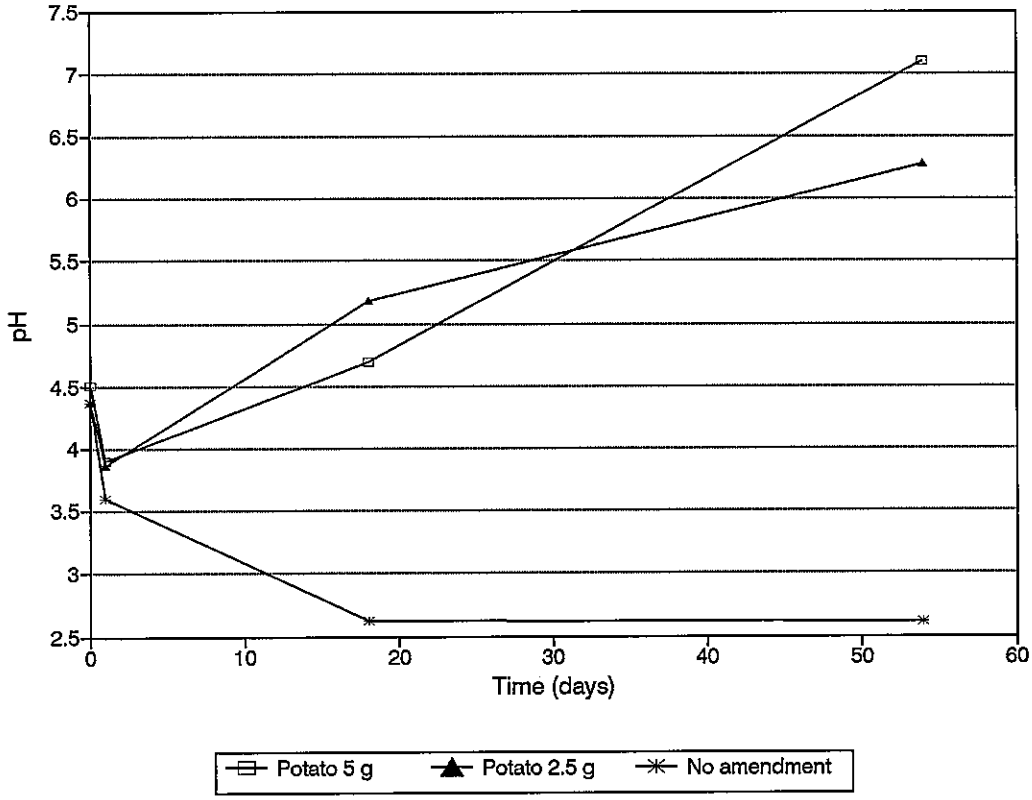


Fig. 6b: Mud Lake ARUM Experiment
Potato jars room temp, conductivity

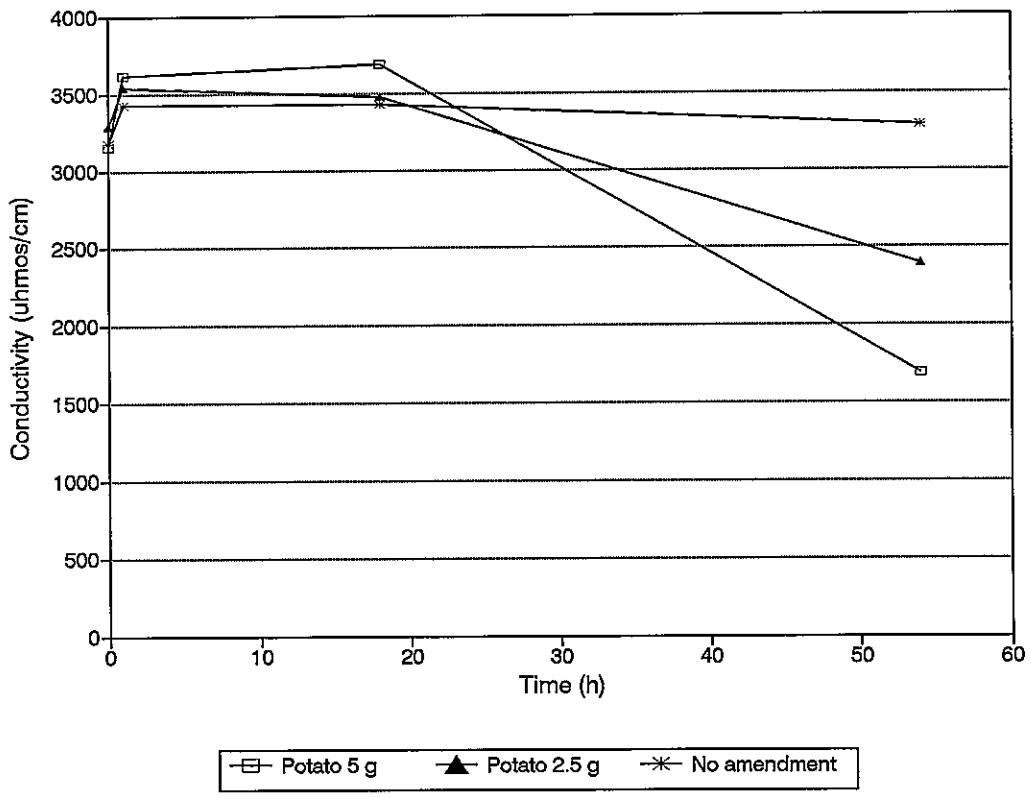


Fig. 6c: Mud Lake ARUM Experiment
Potato jars room temp, Eh

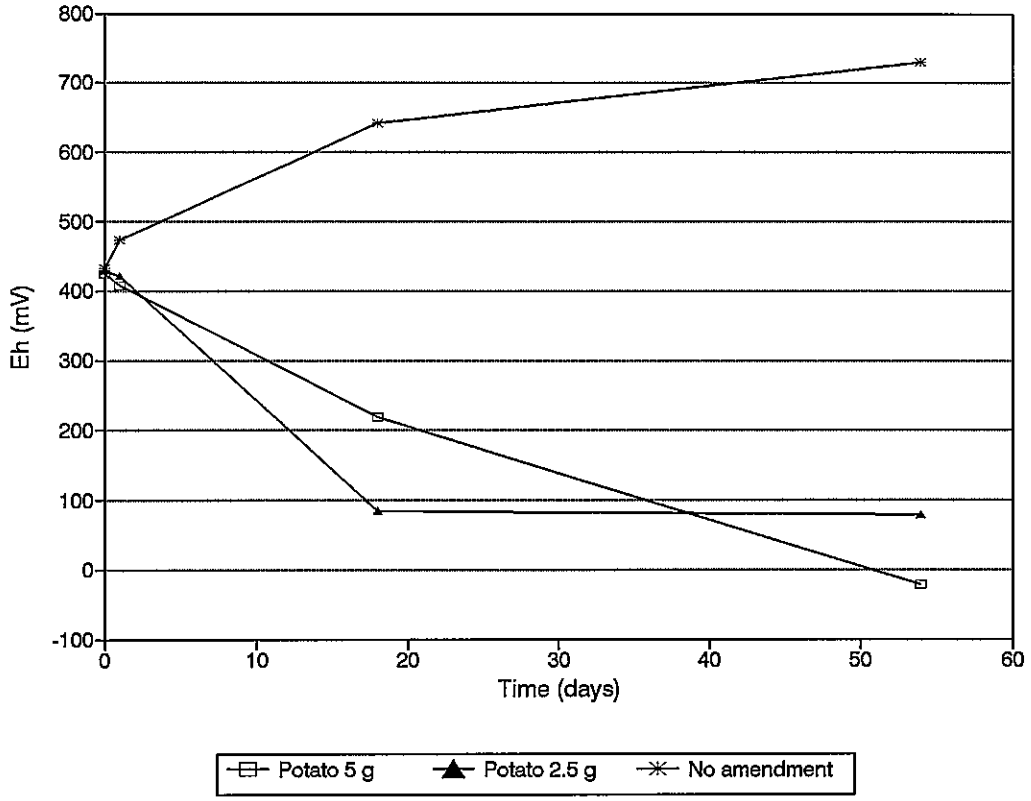


Fig. 6d: Mud Lake ARUM Experiment
Alfalfa jars room temp, pH

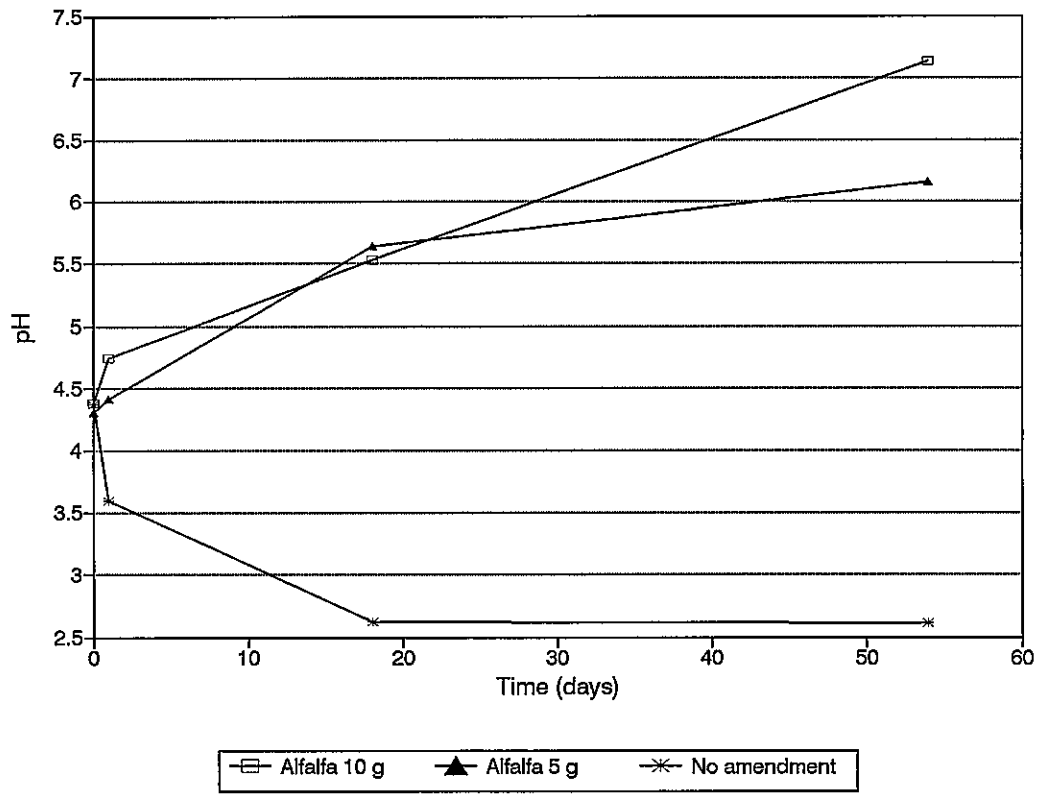


Fig. 6e: Mud Lake ARUM Experiment
Alfalfa jars room temp, conductivity

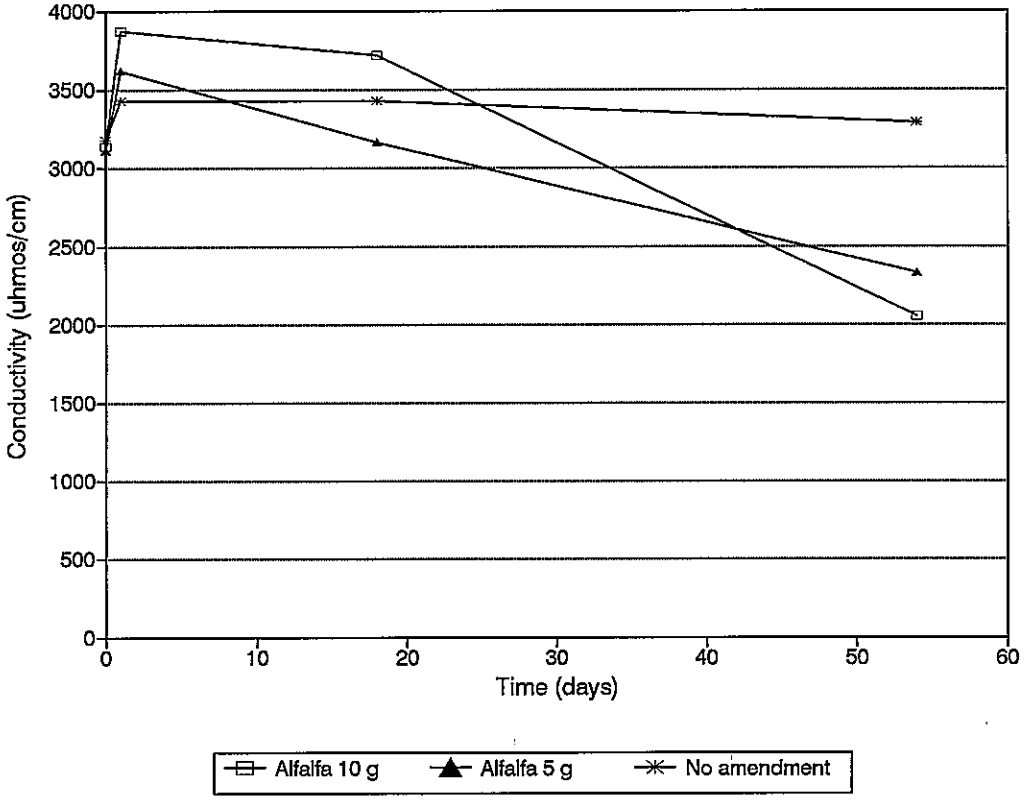


Fig. 6f: Mud Lake ARUM Experiment
Alfalfa jars room temp, Eh

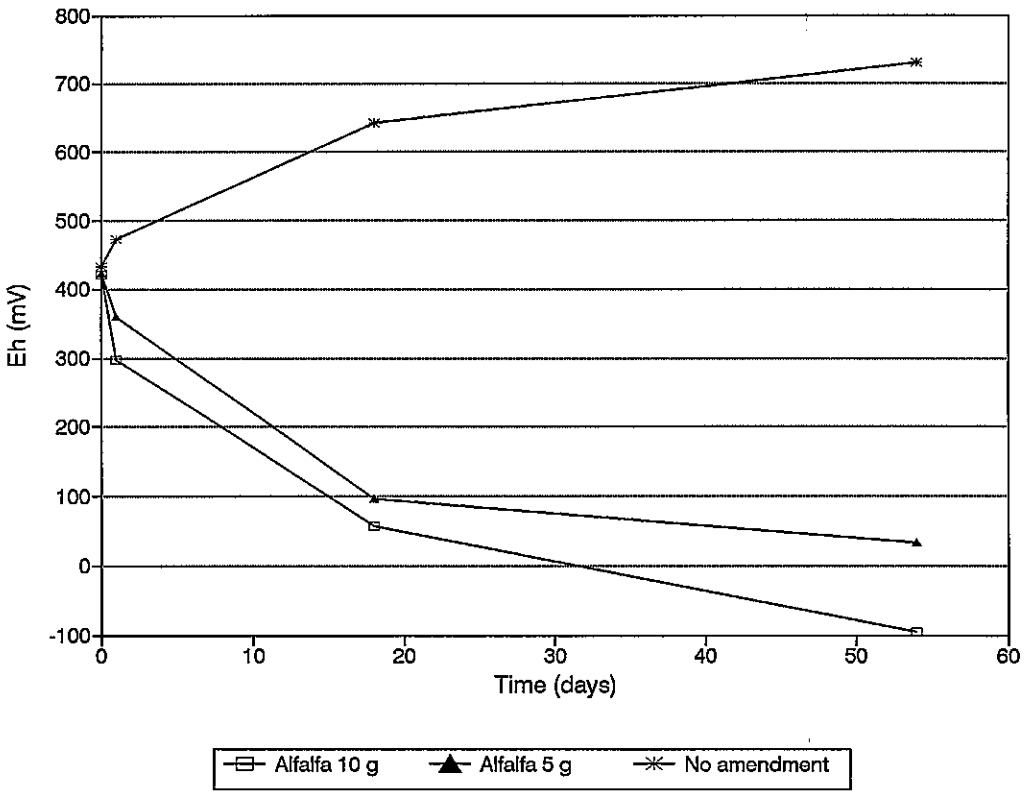


Fig. 7a: Mud Lake ARUM Experiment
Potato jars cold room, pH

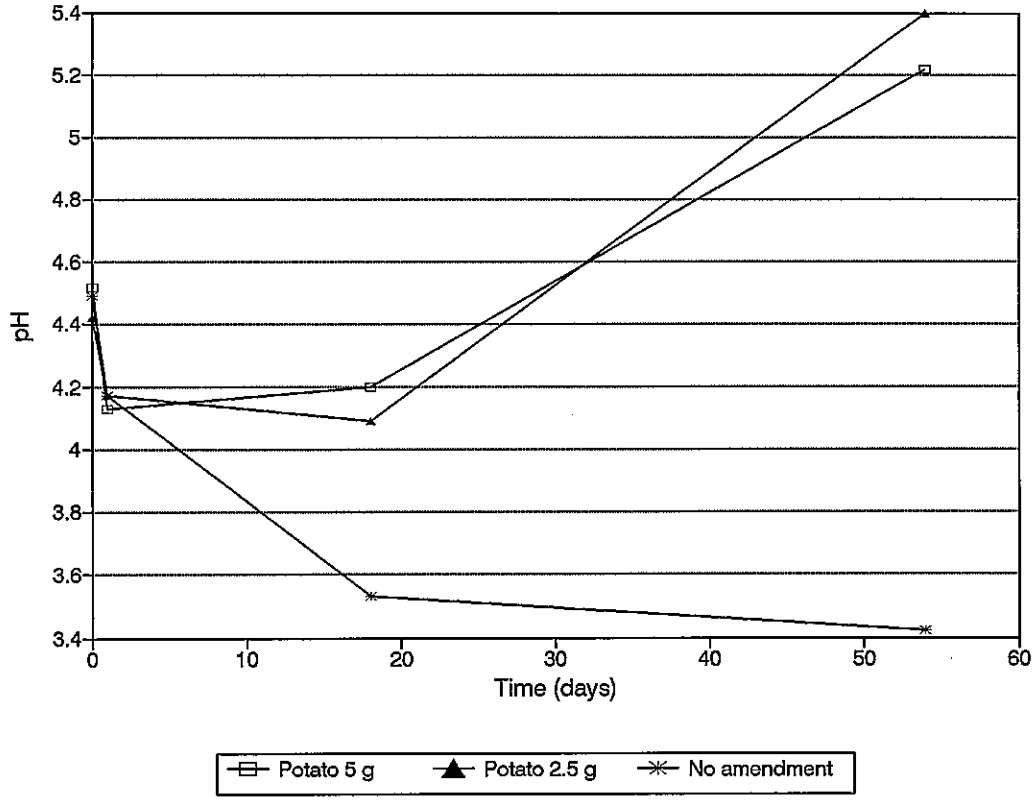


Fig. 7b: Mud Lake ARUM Experiment
Potato jars cold room, conductivity

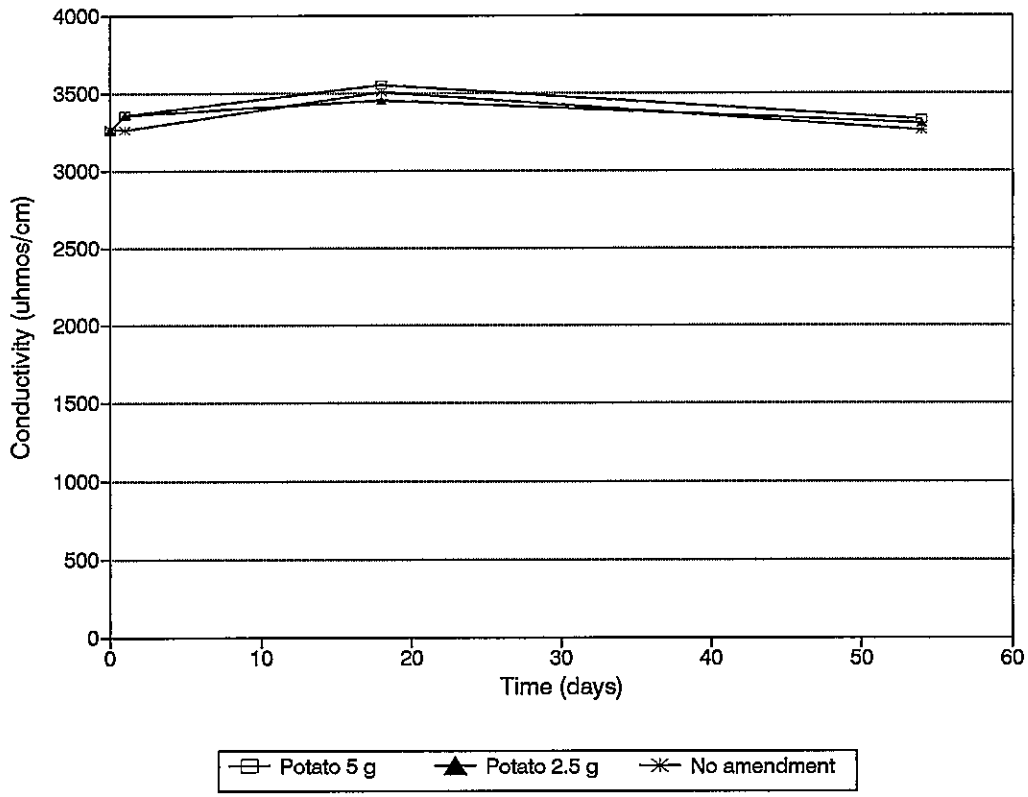


Fig. 7c: Mud Lake ARUM Experiment
Potato jars cold room, Eh

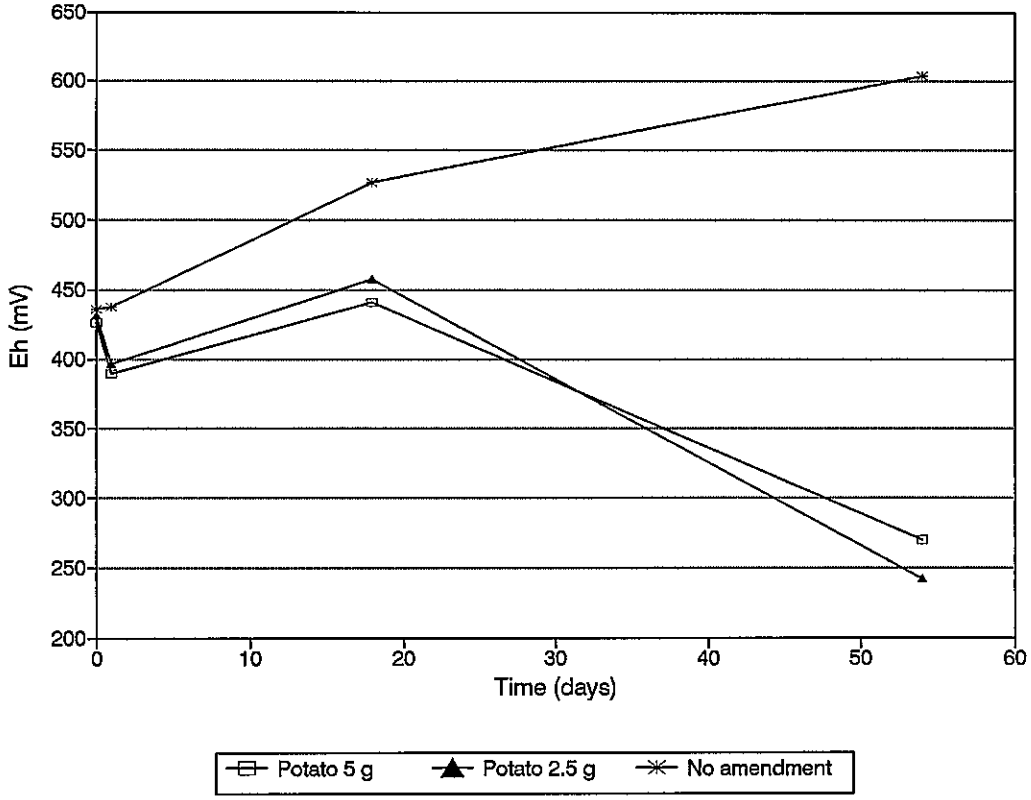


Fig. 7d: Mud Lake ARUM Experiment
Alfalfa jars cold room, pH

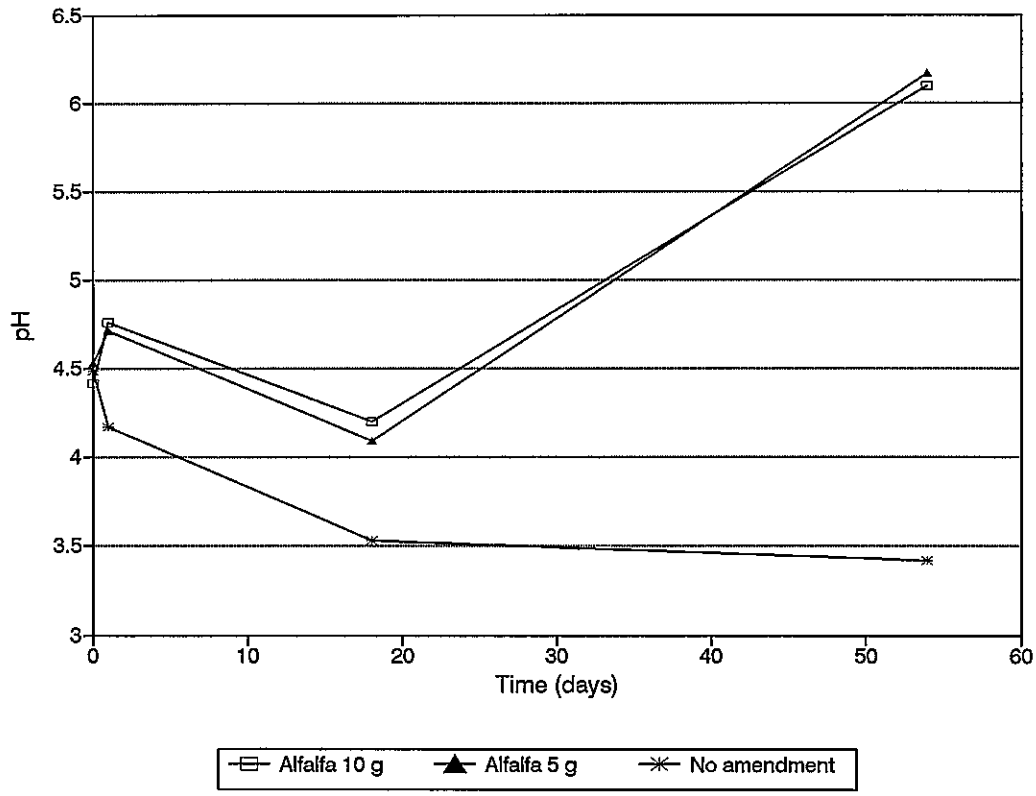


Fig. 7e: Mud Lake ARUM Experiment
Alfalfa jars cold room, conductivity

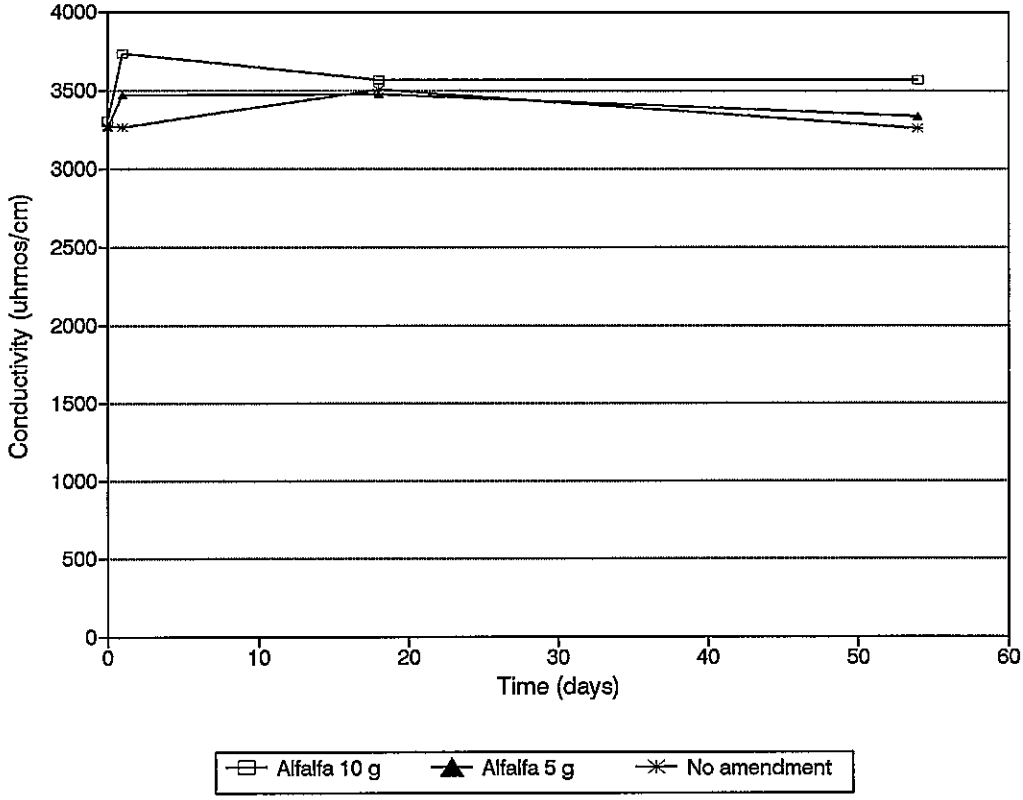


Fig. 7f: Mud Lake ARUM Experiment
Alfalfa jars cold room, Eh

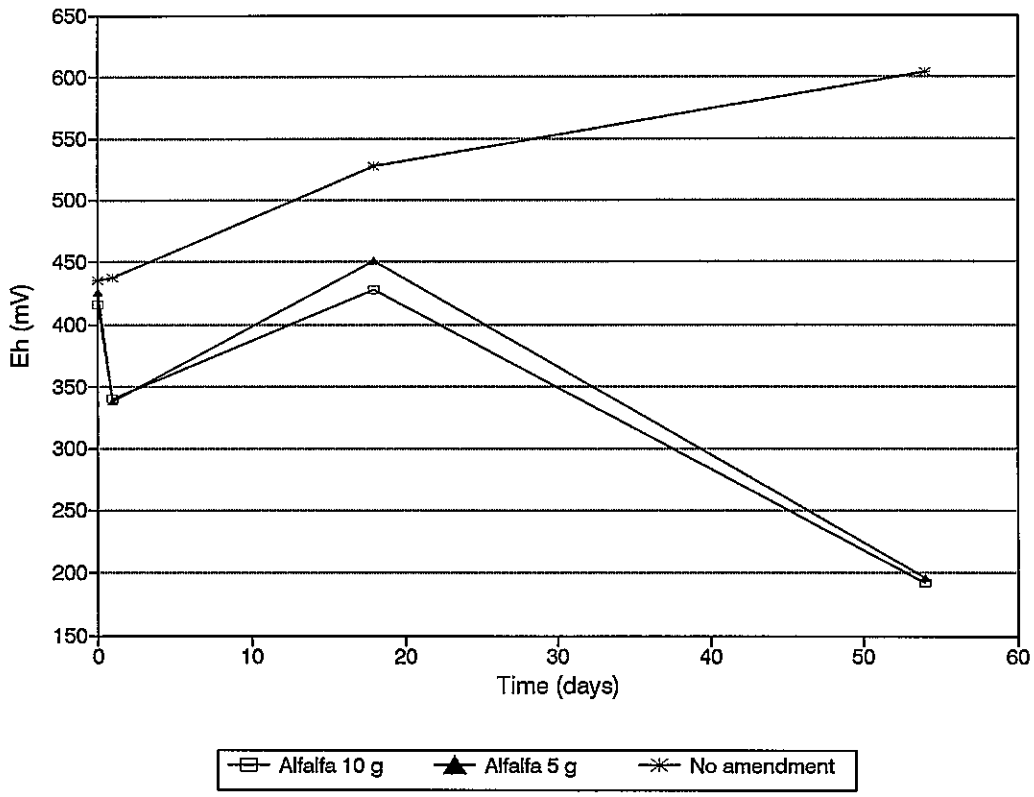


Fig. 8a: Mud Lake ARUM Experiment
Potato jars room temp, pH

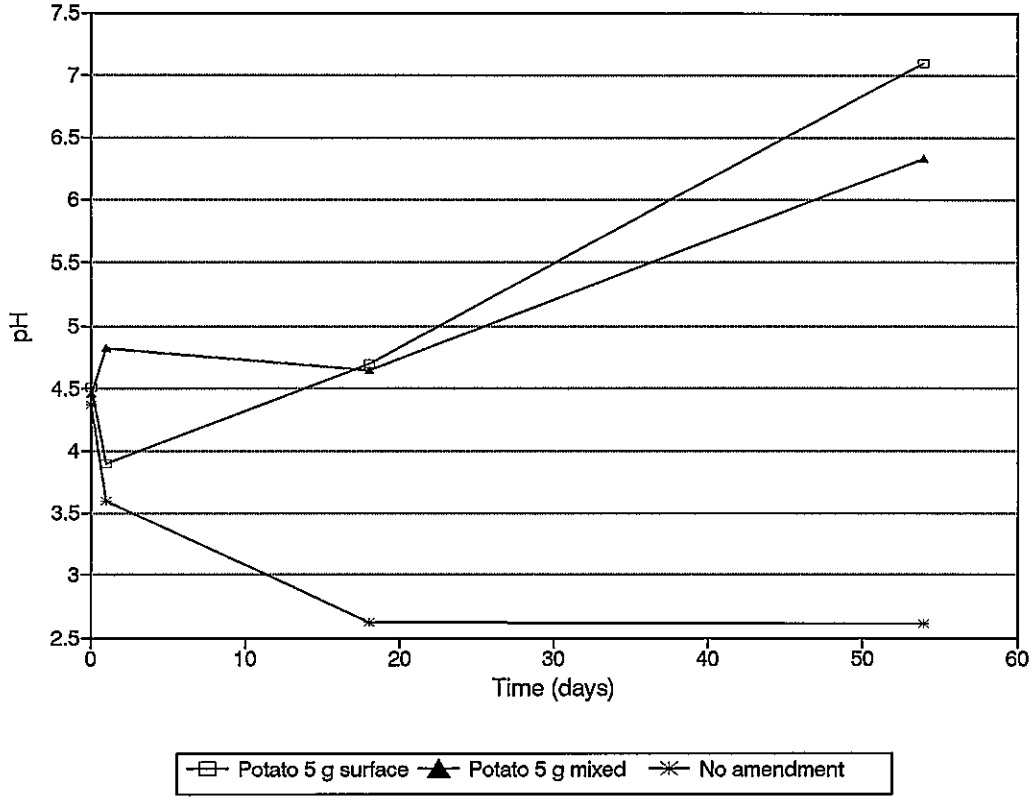


Fig. 8b: Mud Lake ARUM Experiment
Potato jars room temp, conductivity

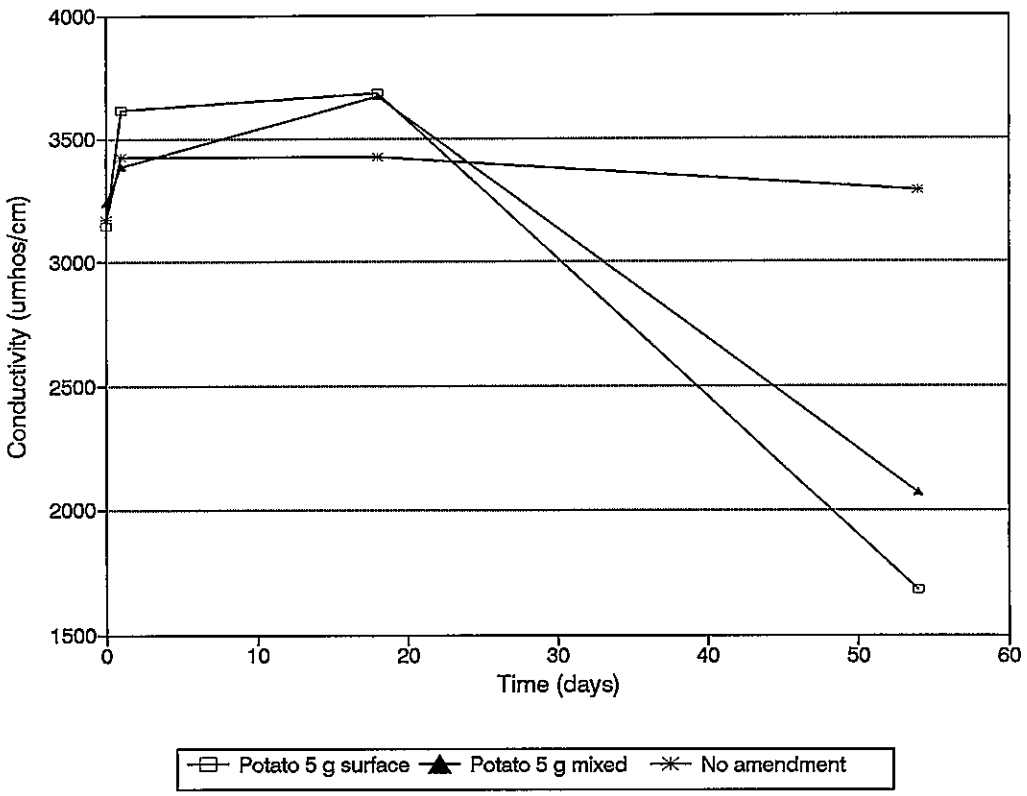


Fig. 8c: Mud Lake ARUM Experiment
Potato jars room temp, Eh

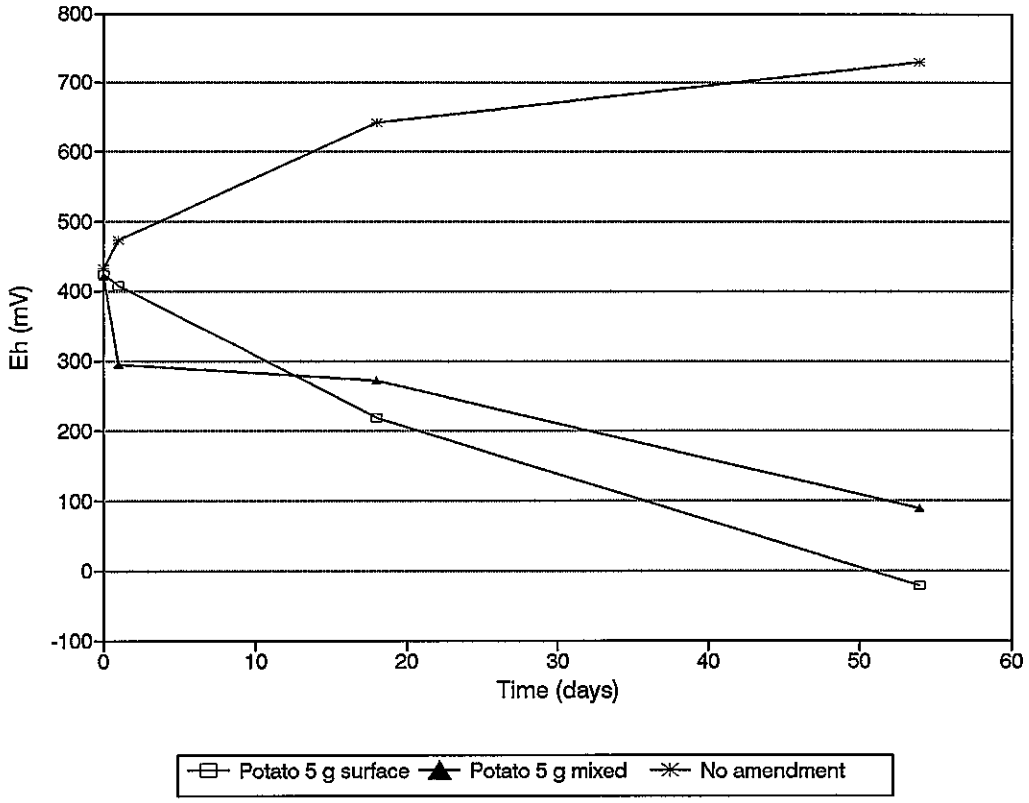


Fig. 8d: Mud Lake ARUM Experiment
Alfalfa jars room temp, pH

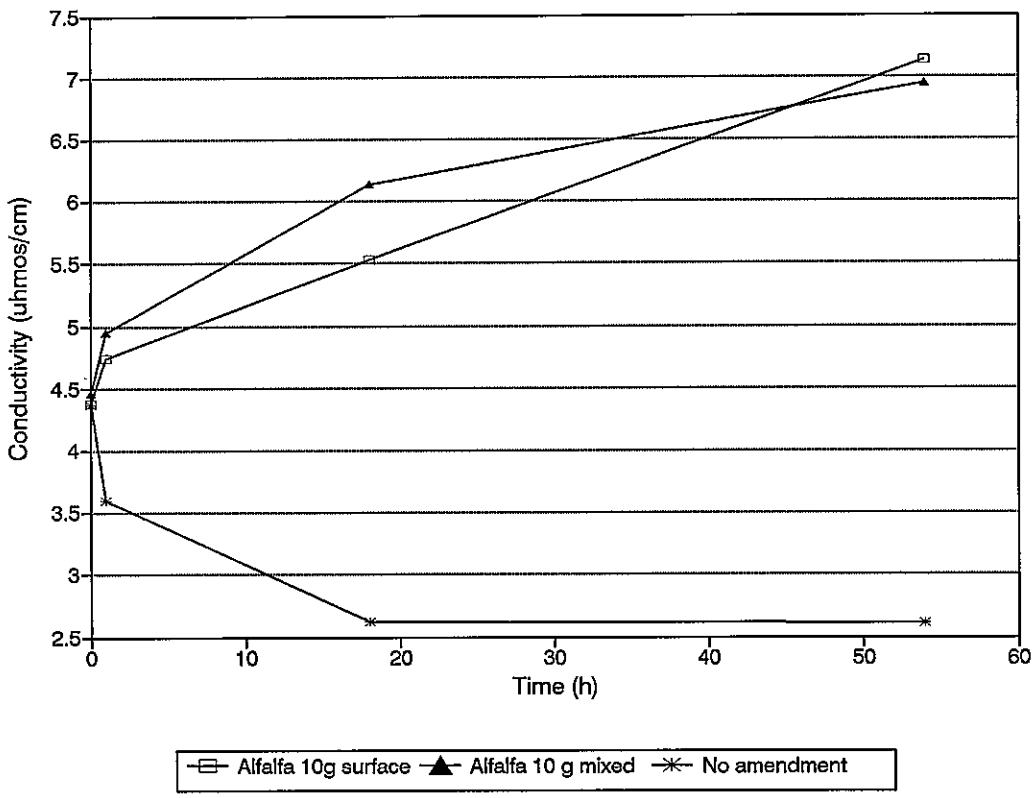


Fig. 8e: Mud Lake ARUM Experiment
Alfalfa jars room temp, conductivity

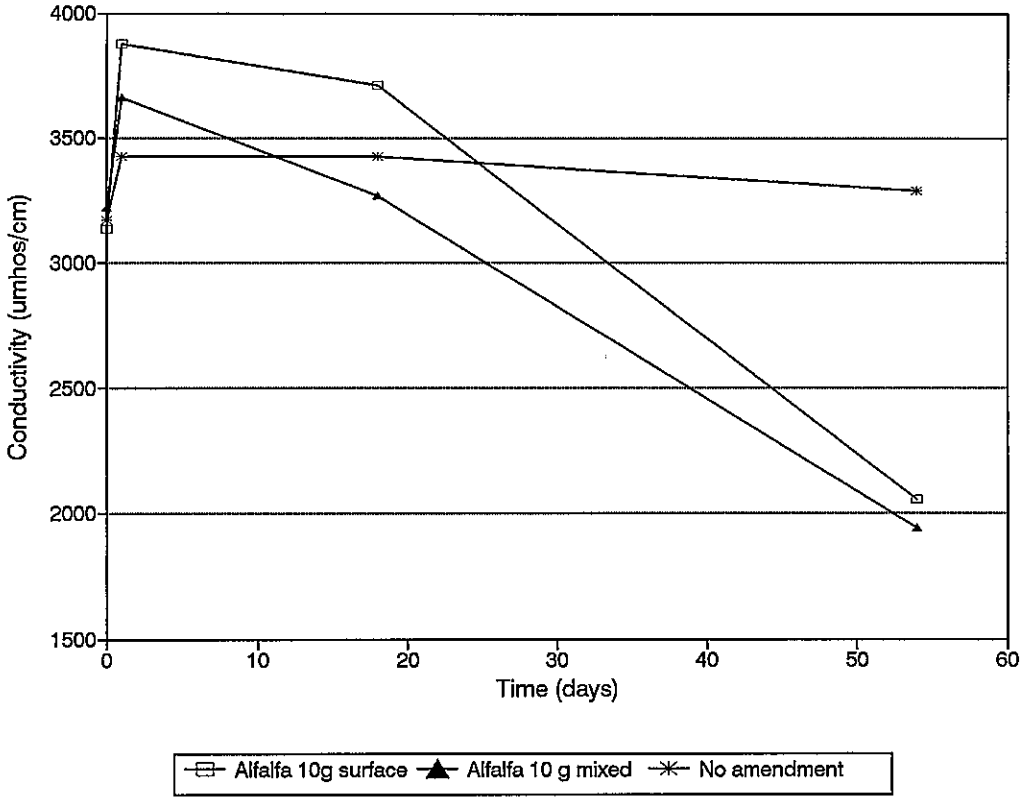


Fig. 8f: Mud Lake ARUM Experiment
Alfalfa jars room temp, Eh

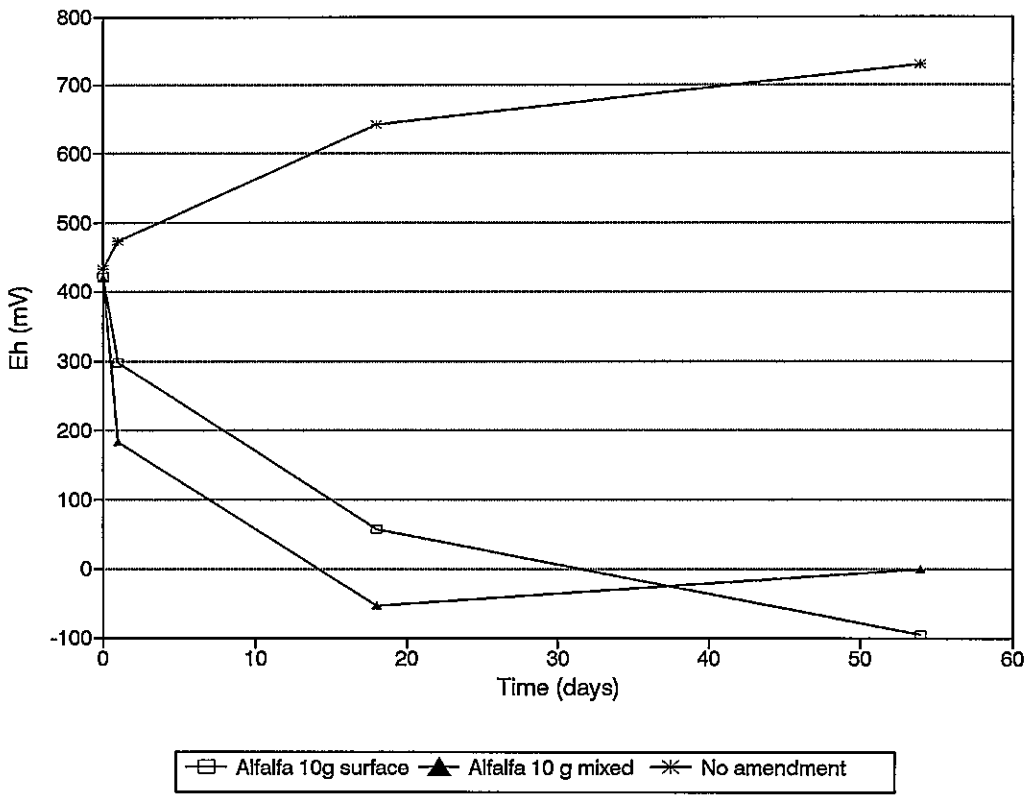


Fig. 9: Mud Lake ARUM Experiment
Acidity titrations,12 days after set-up

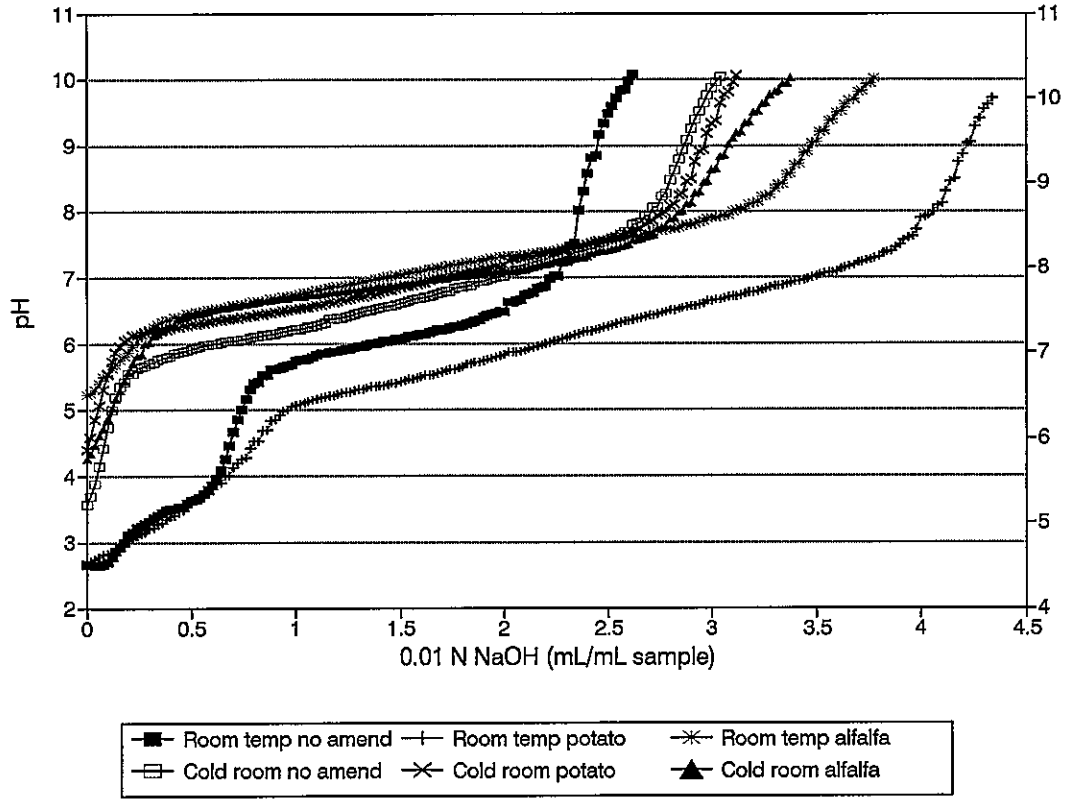


Fig 10: Mud Lake ARUM Experiment
Acidity titrations,18 days after set-up

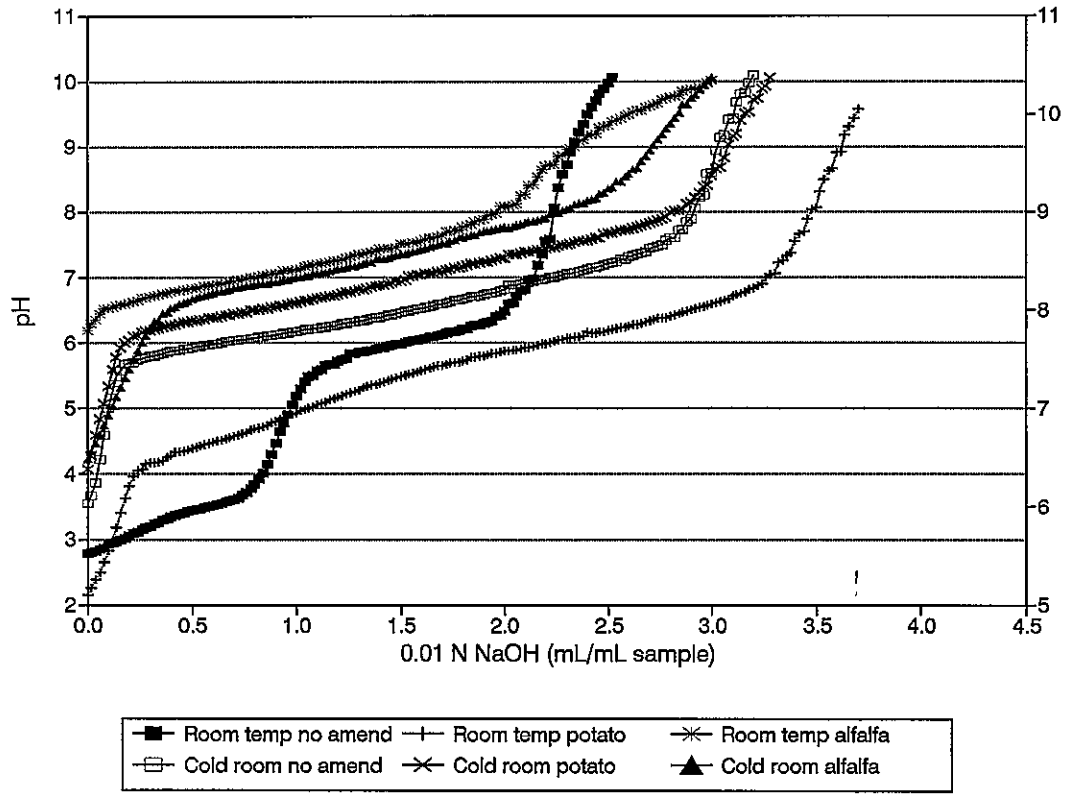


Fig 11: Mud Lake ARUM Experiment
Acidity titrations,23 days after set-up

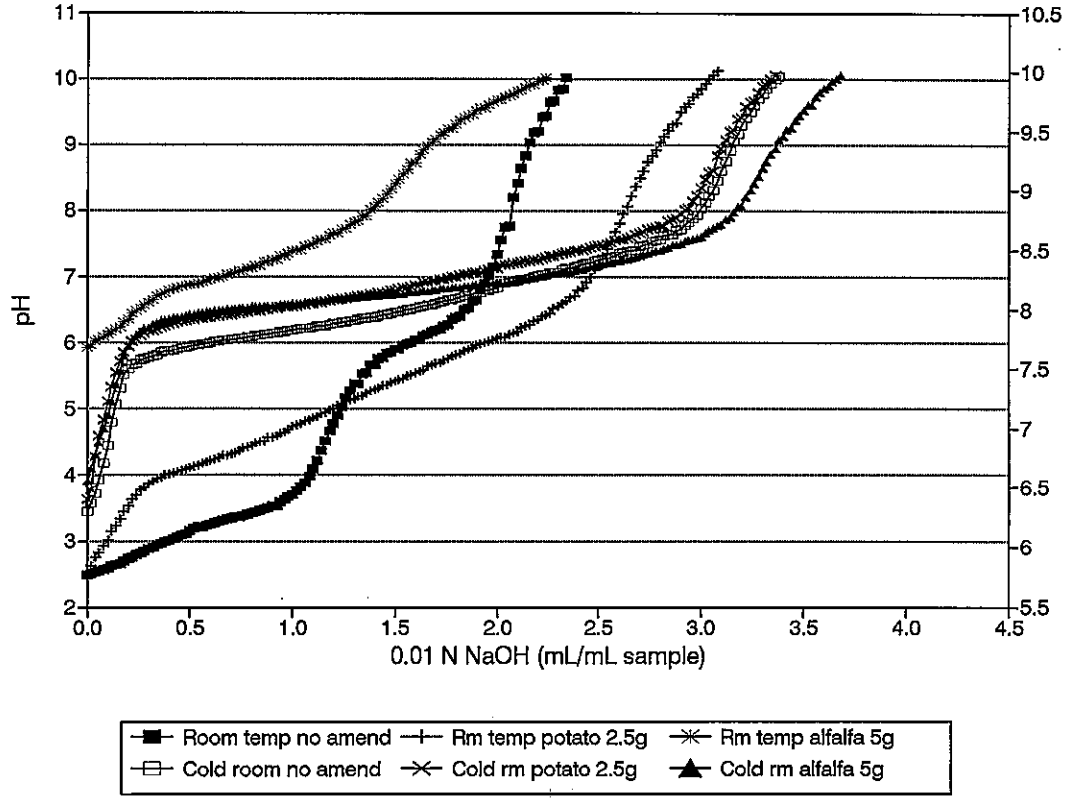


Fig. 12: Mud Lake ARUM Experiment
Acidity titrations,72 days after set-up

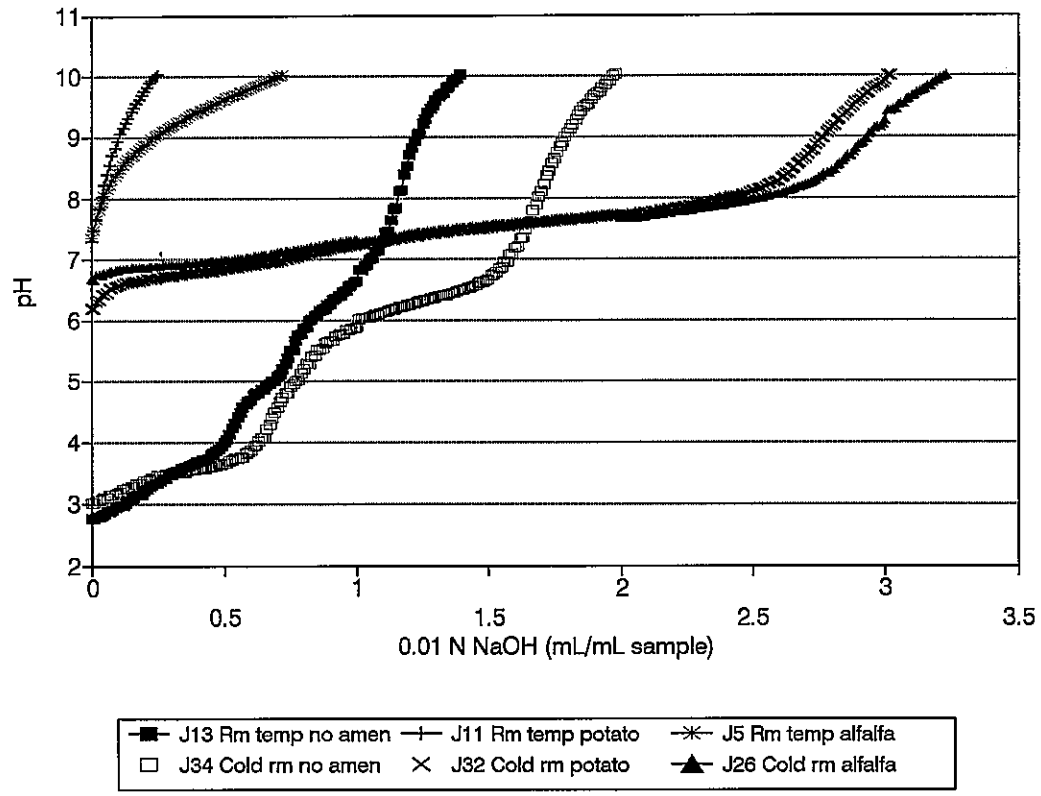


Fig 13: Mud Lake ARUM Experiment
Alkalinity titrat.,72 days after set-up

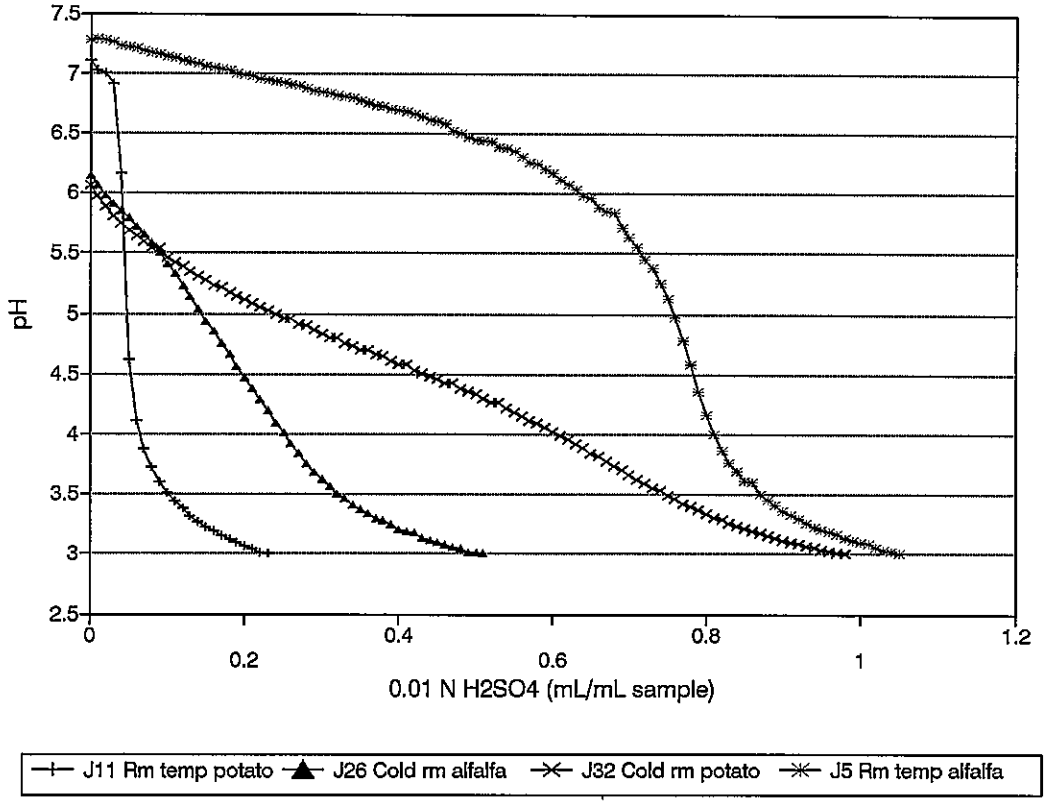


Fig. 14a: Mud Lake, Field Samples
Acidity Titrations, February 26, 1995

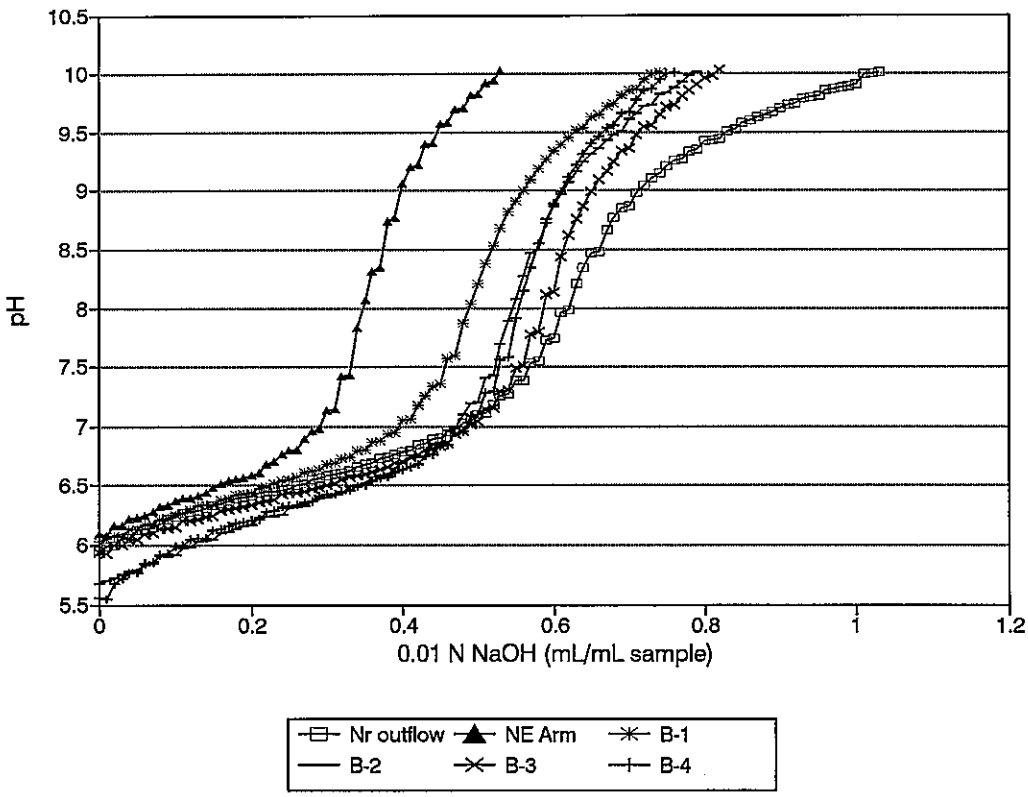


Fig. 14b: Mud Lake, Field Samples
Acidity titrations, February 26, 1995

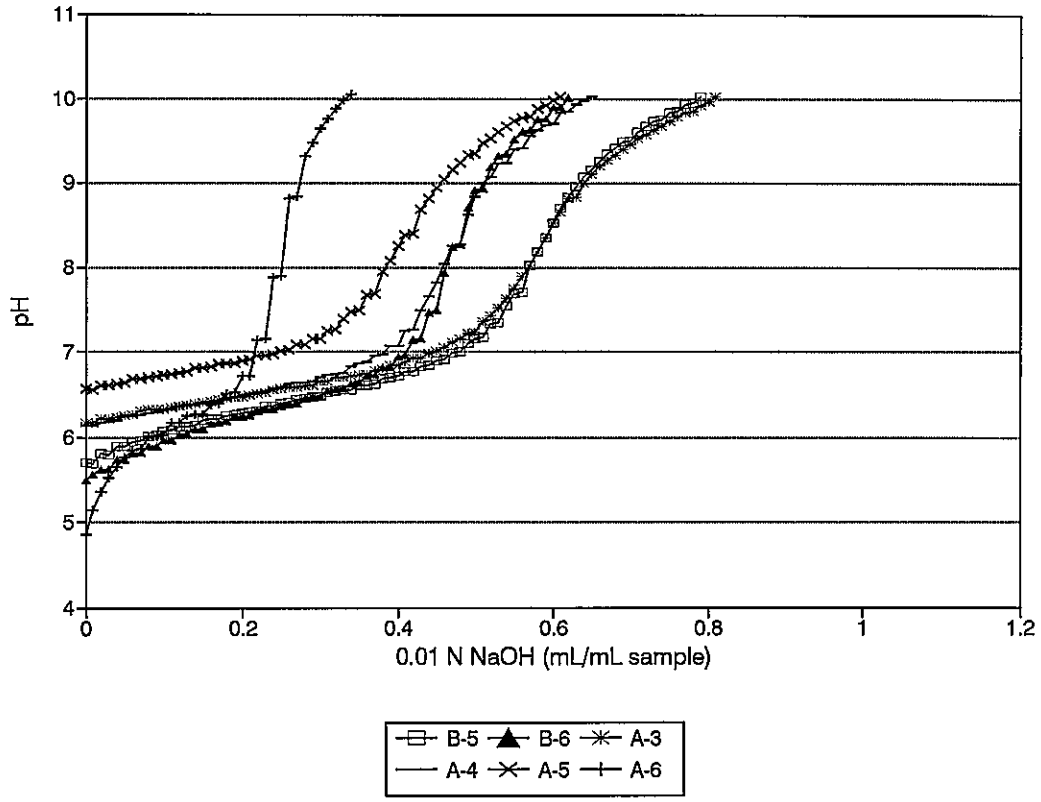
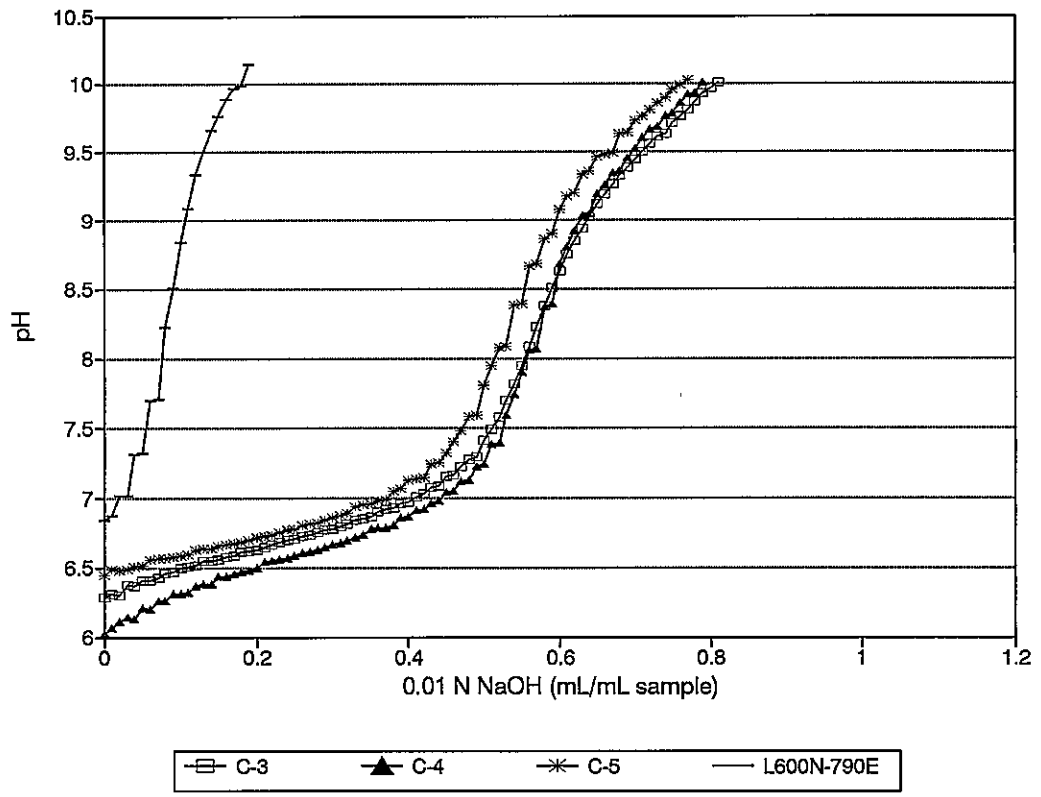


Fig. 14c: Mud Lake, Field Samples
Acidity titrations, February 26, 1995



Biogeochemical Barriers in Mine Waste Restoration - An Ecological Engineering Approach

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<heading1 >Abstract

Most sulphur-containing mine wastes generate Acid Mine Drainage (AMD). AMD, a byproduct of microbial metabolism on weathered rock surfaces can be expected to be an environmental problem for thousands of years. Thus, there is currently much interest in developing passive treatment systems. These passive treatments could serve either in conjunction with, or as a replacement for conventional treatment technologies, thereby reducing or eliminating the need to add chemicals to neutralize the AMD. With current conventional technologies, neutralizing agents are added to the AMD, resulting in metal- laden hydroxide sludges which require further disposal. Just as weathering assisted by microbial activity produce the original acidity in the AMD, passive treatment approaches utilize other micro-organisms to generate alkalinity, raising pH. This in turn leads to the removal of metals from solution through precipitation and adsorption processes. The precipitated metals are relegated to the sediments where, ultimately, they are bio-mineralized, becoming environmentally stable. In this paper we discuss the results from experimental microbial systems (reactors and field tests) being developed to treat AMD under a variety of conditions and mining environments. Removal rates for reactors and field system range from 0.1 $g/m^3/day$ to 3.8 $g/m^3/day$ the metals tested (Ni, Zn, As), for iron from 0.04 to 39 $g/m^3/day$ and for sulphate the removal ranges from the lowest of 1.1 $g/m^3/day$ to 51 $g/m^3/day$.

Ultimately, the treatment capacity of a passive system is dependent on biologically-mediated reaction rates. The results from the experiments suggest that these rates are specific to the chemical characteristics of AMD. The time required for the onset *of* the microbial activity can vary from less then one month, up to twenty months. The suitability of passive treatment systems to a site depends on the hydrological and physical conditions of the waste management area. The two essential design criteria for these passive systems are the retention time of the waste water and the surface area of sediment available for treatment activity.

<heading1>Introduction

Ecologically oriented waste water treatment approaches have been utilized in the treatment of domestic sewage and agricultural effluent for the past 2000 years (Wang 1987). However, in the western world, the ability of ecosystems to remove contaminants from waste waters has only been exploited since the early 1980's (Hammer 1989; Cooper, Findlater 1990; Mitsch 1994).

The generation of acid from many mine waste deposits (waste rock and tailings) has been predicted to continue for thousands of years. AMD is conventionally treated by adding neutralizing agents, usually lime. This treatment results in the generation of hydroxide sludges, which are voluminous and require further disposal. Therefore, operating costs of treatment facilities are long-term economic liabilities for the industry (Orava et al. 1995). Passive treatment approaches for effluent from acid- generating mining wastes are of particular interest to the mining community because: a) the ultimate product is not a sludge with disposal problems, but an environmentally stable (biomineralized) sediment (Ehrlich 1990); b) microbially-mediated and biologically-mediated treatment systems require little or no operating expenses. The evaluation of wetlands to ameliorate Acid Mine Drainage (AMD) began with Wieder and Lang (1984), who reported that coal seepages passing through natural wetlands emerged with a significant improvement in their water quality.

Natural wetlands, however, are not capable of handling AMD input over long time periods. Lane (1990) reviewed the use of natural wetlands to ameliorate AMD. Natural wetlands were those which received AMD, not by design but by default. Sediments were enriched in metals but water quality leaving the wetlands was not improved. These observations were not unexpected. Natural wetlands can only sustain a metal loading rate equal to the biogeochemical removal rates in the sediments.

In the past 10 years, extensive work has been carried out by many workers experimenting with various approaches to constructing and designing wetlands for the treatment of mining effluent. In a recent review of the subject, over 150 publications were evaluated to assemble data on the effectiveness of passive treatment systems (Kalin et al. 1995a). After reviewing the performance data of 35 of these

publications', it became obvious that the design and performance criteria were not standardized. This was to be expected, as passive treatment systems for effluents in the mineral sector, are mainly experimental and are still considered an emerging technology.

For passive systems, two key factors determine performance. The first factor is the microbial activity which prevails in the sediment. The second factor is the settling rate of precipitates/particulates formed in the water as a result of the exchange between water and sediment. Mining waste waters present in comparison to neutral or nutrient enriched water for the sediments, extreme environments. Microbial activity in these extreme environments is probably of a similar order of magnitude. The resulting precipitates /particulates formed, can be expected to be of similar size, and are likely to adhere to surfaces or settle to the sediments at similar rates. The removal of a specific contaminant from AMD will therefore take place at a given rate. If these assumptions are justified, then the question arises what are the critical parameters which affect treatment capacity of a system? These parameters can be determined through a comparison of contaminant removal rates collected in similar experimental conditions, but with different water chemistries. This paper summarizes new data from field tests and laboratory experiments, along with previously reported data, with the objective of empirically defining the critical factors regulating the capacity of passive treatment systems.

< heading 2 > Laboratory Reactor Experiments

Reactor set-up: Most reactor experiments utilize the same principle, i.e. waste water to be treated is contacted in or over a sediment which was collected from the site where passive treatment is being considered. Sometimes the sediment is enriched with organic material, or if no sediment from the site is available, it is created with the addition of readily degradable organic matter.

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1 An error was noted by the author of the publication in Table V (page 371). The units given for treatment rates should read $mg/m^3/min$ not $mg/m^3/day$.

Here we report on reactor studies performed with AMD from five differing locations Canada, Northern Quebec (base metals), Central Ontario (nickel/copper), Central Ontario (uranium), Northern Ontario (base metals), Northern Saskatchewan (uranium). Constructed sediments were required when passive treatment was considered for use in an open pit and a tailings pond, where no natural sediment was present. This was the case for effluents from the base metal mine in Northern Quebec, the nickel/copper and uranium mines in Central Ontario. If the AMD to be treated was very reactive (prone to rapid changes in oxidation), i.e. it emerges from the tailings dam in a reduced form, the reactors had to be set up on site. This was the case for the 200 L drums used in the experiments in Central Ontario (Table 1). These reactors were filled with flax and hay to create a sediment structure. The void space was then filled completely with seepage. All other reactors were run in the laboratory.

For the Northern Ontario site where microbial treatment is being considered for a shallow lake with natural sediment, the reactors were run both in a cold room and at room temperature. The cold room provide temperatures prevailing in the sediment in lakes. The temperature effect on the microbial activity was assessed by comparing the removal rates obtained from these reactors.

Natural sediment in reactors and field experiments can be supplemented with potato-waste which serves as an easily degradable carbon source. The reactors in Northern Ontario consisted of 0.85 L of sediment and 0.85 L of seepage. In Northern Saskatchewan, where a bog/muskeg is being considered as the site of a passive treatment system, the reactors consisted of 0.5 L of sediment and 1.5 L of seepage. Reactors were monitored either sporadically (Central Ontario) when located on site or regularly when in the laboratory. Water samples, removed from the reactors, were either measured in the field or both in the field and laboratory, to ascertain changes occurring during transport. The pH, Eh, electrical conductivity, and acidity/alkalinity were recorded. Changes in these parameters indicate the onset of microbial activity. When changes were noticed, another water sample was taken, filtered through 0.45 μm filters and acidified to pH 1 or less. The filtered samples were then submitted to a certified laboratory for chemical analysis (Inductively Coupled Plasma Spectroscopy).

<heading3>Results and Discussion

The results of reactor sampling are shown in Table 1. This table summarizes water characteristics before and after the onset of microbial activity in reactors studied in Canada over the last 6 years. The row labelled Period of Observation represents that time which elapsed from the beginning of the experiment until significant water quality improvements were noted. This time ranges from less then one (1) month to twenty (20) months. The chemical characteristics of the AMD treated from the different sites varied widely. For example, acidity ranged from 158 to 4250 mg/L $CaCO_3$ equivalents. Equally large ranges in the concentrations were noted for other elements. The seepage from Northern Quebec with very high acidities required 16 months until a significant reduction in acidity was noted (4250 mg/L $CaCO_3$ equivalents to 405 mg/L $CaCO_3$ equivalents). The pH increased from 2.4 to 7.2 over this time span. Zinc concentrations decreased from 569 mg/L to <1 mg/L, while 3.8 mg/L copper and 85 mg/L aluminum were removed (not given in Table 1). The reactor, filled with seepage from the Central Ontario tailings, after 20 months in the field, had 3035 mg/L $CaCO_3$ equivalents of alkalinity, up from an original acidity of 1197 mg/L $CaCO_3$ equivalents. Over 20 months, the pH had risen from 5.3 to 7.0, the iron had precipitated and was reduced from 281 mg/L to 1.2 mg/L. Nickel concentrations had dropped from 61 mg/L to <1 mg/L. The seepage from the uranium operation in Central Ontario, had a level of acidity similar to the nearby base metal seepage, but with significantly lower sulphate concentrations (879 mg/L as compared to 3663 mg/L). The field-based reactor produced water chemistry changes after just 4 months (acidity reduction from 1014 mg/L $CaCO_3$ equivalents to 382 mg/L $CaCO_3$ equivalents).

Although the seepages in Northern Quebec and Central Ontario required about 16 and 20 months, respectively, to show significant changes in water chemistry, they did finally support a microbial population. This suggests that even very strong acid mine drainage with high sulphate and metal concentrations will eventually support microbial activity.

The seepage from Northern Saskatchewan, had a low acidity (158 mg/L $CaCO_3$

equivalents) and a relatively high pH for acid mine drainage, with a value of 4.1. The water in the reactor showed improvements in quality over a relatively short period of 1.3 months. From these observations it is suggested that the time required to alter the chemical composition of water through sediment-bound microbial processes is related to the chemical composition of the acid mine drainage.

The effect of temperature on the time of microbial activity onset were investigated in reactors containing sediment from a lake in Northern Ontario (Mud Lake). One reactor was kept a room temperature (22° C), while the other was kept in a cold room (5° C). The cold room temperature simulated the temperature found in the sediments of the lake year-round. Within 23 days, the water in the room temperature reactor had an acidity which was half that of the original water 2255 mg/L $CaCO_3$ equivalents to 1234 mg/L $CaCO_3$ equivalents. This was mainly due to the removal of iron, the concentration of which dropped from 1140 mg/L to 615 mg/L. The reduction in zinc concentrations, from 81 mg/L to < 1 mg/L, was due to co-precipitation of zinc with iron, as the pH of 5.9 was not high enough for zinc hydroxide precipitation.

In the cold room reactor, with the exception of manganese, similar reductions in all the parameters were noted after 2.8 months. Thus, the differences in the onset time appear to be temperature dependent, much as microbial activity is temperature dependent. Based on these temperature results, and the fact that field sediment temperatures rarely exceed those simulated in the cold room, a minimum retention time of 3 months is required to implement the treatment approach in the lake.

<heading2> Field Test Experiments

The removal rates obtained from the reactor experiments provided a first assessment of the applicability of passive systems to a specific AMD chemistry. Field tests provide information on the contaminant removal rates under non-static conditions and with seasonal variations.

Field tests were carried out in 5 mining locations in Canada. The first was the copperhickel tailing seepage in Central Ontario. The second were seepages from an old coal waste rock dump in Nova Scotia. The third and forth were from a site in

Newfoundland, water in an open pit and from a seepage from a waste rock pile. The fifth was a seepage from waste rock pile at a uranium mine in Northern Saskatchewan. The results reported here cover a period of 4 years.

Field test site descriptions: In Table 2 field test results are summarized for the five different field test locations. The setup for all field tests was essentially the same. A containment structure was built, which increased residence time of the effluent to be treated. The structures were constructed of earthen berms or Fabrene curtains suspended from floats. The bottom of the curtain was secured to the sediment with weighted chains.

At site #1, an engineered field test system was constructed for the nickel/copper seepage from a tailings dam. It was engineered to provide a controlled flow ranging from 0.1 Llmin to 1.5 Llmin. Part of the seepage was bypassed into a series *of* 6 cells, where flow was controlled by two valves. In the first two cells of the system, the seepage oxidized and precipitation of iron hydroxide took place. The acidified seepage then entered two cells with constructed sediments. A floating cattail cover was installed over the latter two treatment cells. Details of this system are given in Kalin (1993). The retention time was calculated from the volume of the treatment cells and the flow.

At site #2 coal seepage from an abandoned coal waste rock pile was enclosed in Fabrene covering an area of 100 m^2, containing about 40 m^3 of water. A floating cattail cover was installed on the enclosure. Organic amendments (alfalfa pellets and straw) were added over a dead bog sediment consisting of muskeg with iron hydroxide precipitate. The flow into this cell was uncontrolled, being high during rain events, and very low at other times. The flow estimates are averages, based on infrequent samplings during heavy rains and dry periods.

The test conditions for the zinclcopper operation in Central Newfoundland consisted of limnocorrals (volume = 34 m^3) in an abandoned open pit (site #3). The results reported here are those from the limnocorral which was amended with peat and alfalfa hay. The results from the complete series of experimental limnocorrals are given in Kalin (1992). The limnocorral represented essentially stagnant conditions, i.e. water entered into and left the enclosure only with seasonal fluctuations in water level in the

pit. The water level fluctuated annually around 0.15 m. At the same site, seepage from a waste rock pile entered a peat bog with diffuse flow (site #4). A series of three shallow ponds were excavated in bog with distinct inflows and outflows. The ponds were amended with straw, and although the inflow was not well defined, measurements of flow volume were made sporadically and were used to calculate a theoretical retention time.

The enclosures in Northern Saskatchewan (site #5) surrounded a sediment area of 2.4 x 2.4 m in a muskeg and were amended with alfalfa pellets. The water depth in these wetlands varied with the season, about 0.5 m. The sediments in these enclosures have been extensively studied to identify the chemical form of the contaminants in the sediment and detailed chemical analysis were carried out to interpret the microbial interactions between sediment and water (Smith et al. 1993; Fyson et al. 1994; Kalin et al. 1995b).

<heading3>Results and Discussion

In Table 2 the field system dimensions and their retention times are given. Concentrations of acidity, iron, sulphate and various metals are given for the systems either as the water entering the system (#1 and #4) or prior to treatment start. The differences in the concentrations of the elements considered, represent reductions in absolute terms. Although the reductions are generally greater then 50%, the retention times range from 3 to 6 month. The removal of contaminants essentially starts after the first season, regardless of the size of the system or the volume treated. The absolute removal again suggest, similar to the reactors (representing conditions in the sediment), that some differences between sites might be due to the chemistry of the AMD.

The data presented in Table 1 and 2 are used to derive removal rates in $g/m^3/day$ (Table 3). For acidity, which is a combined variable representing the removal of iron and metals from the water, the rates for field systems #1, #2, #3 and #5 are for all parameters in ranges differing only by a factor of 10, with the exception of system #4, where removal rates are a factor of 100 higher.

The higher rate of acidity removal of 2.8 $g/m^3/day$ for the coal seepage in the field is due to the fact, that acidity is including removal of aluminium which is present in higher concentrations than in the other seepages. The sulphate removal rates range from 1 $g/m^3/day$ to **435** $g/m^3/day$. The high rate is likely due to the peaty nature of this system constructed in a peat bog. Although the zinc removal with 71 $g/m^3/day$ in this system is high and the iron removal is negligible, zinc removal does not take place through microbial action alone here. Extensive algal growth is present in this system, as it is the only one of the field systems which does not have a vegetation cover, due to its shallow nature. The removal rates of the metals are generally in the same range, as might be expected, given the removal mechanisms.

The removal rates for the field systems can also be calculated with respect to the area of sediment available system, from the data in Table 2. The ranges which consider removal per m^2 of system display the same orders of magnitude as those based on the volume of the system (calculation not presented in Table 2). For example in the flow through system #1 and in system #2 the removal per m^2 or per m^3 is essentially the same. In the other three system the resemblance is between area and volume removal per unit time is that the highest removal is of the same parameter, but the effectiveness is different. It does suggest, although only indirectly that indeed the sediment is the key factor with its microbial reactions in the treatment approach.

Initial design criteria for the construction of wetlands were based on the performance of systems operating in the Tennessee Valley Authority (TVA) region (Brodie **1991).** Wetland size was based on the area estimated to remove a specific quantity of iron to an acceptable level. Hedin and Nairn (cited in Smith et al. **1993)** have suggested criteria for selection of wetland type (aerobic or compost) and sizing based on data from a variety of constructed wetlands for mine drainage treatment. Where the water is net-alkaline, passive systems with aerobic wetlands are recommended with sizing based on 20 $g/m^2/day$ Fe or **0.5** $g/m^2/day$ Mn. For net-acidic waters, systems with compost wetlands are recommended with sizing based on **5** $g/m^2/day$ acidity and **0.5** $g/m^2/day$ Mn. This pragmatic approach to siting a wetland does not consider the microbial activity of the sediment, but utilizes the adsorption capacity of wetland areas. The data from the field systems presented here, where the microbial activity

is optimized through a floating vegetation cover, the removal rates are probably more reasonable guidelines for system design.

The removal rates of the laboratory reactors are expected higher than those in the field system as they represent conditions closer to inside the sediment. The concentrations gradient which is established between the water body to be treated and the sediment providing the treatment is probably a big factor contributing to treatment effectiveness. As iron and sulphate reductions are the dominant microbial processes, which will be supported by mining effluents the interplay between those two is possibly expressed in the generally lower iron removal rates than those of sulphate removal. Metals removal rates are again somewhat lower, as other processes such as adsorption and coprecipitation will paly a major role in the removal.

<heading2> Organic Substrates for Sediment Construction

Many different organic materials have been used as sources of carbon and electron donors for microbial processes in AMD treatment systems. It is widely recognized that for large scale use these materials need to be low cost, locally available and readily degradable to compounds usable by' anaerobic bacteria. The materials also should last a long time to minimize the frequency of addition, while breaking down to small organic molecules at a rate consistent with the optimal treatment of AMD.

Straw has been widely used (Bechard et al. 1995), as an organic amendment alone or in combination with limestone and manure. Mushroom compost has shown to be more effective than straw alone or peat (Wieder 1992) but some of the effectiveness of these systems has to be attributable to dissolution of limestone contributing alkalinity and not decomposition of organic material, per se.

Peat is effective for metal removal (Couillard 1994) due to its cation exchange and metal complexation capacity and the large surface area provided, not necessarily because of its carbon content as energy source for anaerobic bacteria. Peat is intrinsically recalcitrant to degradation, being composed mainly of lignin derivatives and in the presence of AMD it will decompose extremely slowly, if at all.

More readily degradable materials have also been employed. For example, Borek et

al. (1995) tested the use of cheese whey to augment sulphate reduction in wetlands receiving AMD. Although this material is an excellent substrate for sulphate reduction, it was not very effective in the field, perhaps because it was washed out or not available to sulphate reducing bacteria. Eger and Wagner (1995) found that composted yard waste and municipal compost were effective in a field system designed to treat AMD anaerobically. Waybrant et al. (1995) also found that complex substrate mixtures were most effective for AMD treatment in anaerobic conditions. For all the systems discussed in this paper, potato waste from a french fry manufacturing plant was used alone or together with alfalfa hay and or pellets (guineapig or horse feed). Potato waste contains 60% starch which is readily broken down in aerobic and anaerobic conditions to substrates (e.g. volatile fatty acids) for sulphate reduction.

Kalin and Smith (1992) installed floating cattail/ vegetation rafts over a number of field test systems as discussed in this paper with the exception of site #4. In addition to providing a cover to minimize wind induced water mixing, these rafts provided a large part of the carbon and energy requirements for the alkalinity generating microbial processes in the form of primary productivity. Whether the decomposition of litter from such growing wetland plants can provide all the organic substrates required for a truly self-sustaining system has yet to be established. It is certainly desirable to use locally produced carbon as this will reduce maintenance requirements and provide a more environmentally attractive solution.

<heading1>Conclusion

Although the removal capacity of the microbially based systems are generally met with scepticism, they have their place as a containment approach. The data summarized in this paper do indirectly demonstrate that ,depending on the site conditions, both hydrologically and chemically, reductions in contaminants leaving the site can be achieved.

The microbial treatment approach is associated with precipitation cell for oxidation of Fe(II), followed by hydrolysis and precipitation of $Fe(OH)_3$, which are not discussed in

this paper. The field systems #1, #2 and #3 discussed in this paper have precipitation/oxidation cells installed.

This precipitation / oxidation process reduces the pH (typically to around 3) but serves to remove the iron (with some co-precipitation of other metals) which also represents a large proportion of the acidity. This results in an effluent stream with little iron. This has two advantages. Iron precipitates may clog up the surfaces of added carbon (e.g. straw), preventing decomposition and adsorption processes. Secondly, with a high percentage of degradable carbon available (through the additions or algal growth, and little iron, the microbial ecological balance is shifted in favour of sulphate reduction. With little carbon and high iron concentrations, microbial iron reduction is favoured, which although alkalinity generating, does not provide sulphide required for precipitation of metal sulphides, and increases metal loading through dissolution of $Fe(OH)_3$. Iron reduction has therefore been considered detrimental to **AMD** treatment (Wieder 1992). We suggest, that passive treatment approaches which do not consider water chemistry changes due to iron oxidation / reduction in the design stage as unrealistic.

The results of field tests lead to the assessment of the contaminant removal capacity in relation to annual contaminant load (flow **x** concentration) to be treated. The area of sediment available for treatment within the waste management area determines the design of the system once it is found suitable for scale up. With both reactor and field test results at hand, the treatment approach can be assessed within the site specific hydrological, climatological and geochemical characteristics of the location where it is to be used.

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Location	Central'' Ontario		Central* Ontario		Northern (22°C) Quebec		Northern (22°C) Ontario		Northern (5°C) Ontario		Northern Saskatchewan	
AMD **Type**	Cu/Ni		U		Cu/Zn		Cu/Zn/Pb		Cu/Zn/Pb		U	
Period of observation (months)	8 - 20		0 - 4		0 - 16		0 - 0.7		0 - 2.8		0.1 - 1.3	
Surface Area (cm^2)	3019		3019		707		125		125		57	
Volume (L)	200		200		22.7		1.7		1.7		2.0	
Substrate	Flax + Straw		Flax + Straw		Flax + Hay		Potato waste		Potato waste		Potato waste	
Location/Time	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
Alkalinity (mg/L)	146	3035	-	-	-	-	-	-	-	-	-	-
Acidity (mg/L)	1197	301	1014	382	4250	405	2255	1234	2255	1302	158	11.6
pH	5.3	7.0	3.3	5.8	2.4	7.2	5.7	5.9	5.7	5.8	4.1	7.3
Sulphate (mg/L)	3663	567	879	33	5760	87	3330	2265	3330	1860	650	78
Cadmium (mg/L)	N/A	N/A	N/A	N/A	2.1	<1	<1	<1	<1	<1	0.21	0.01
Iron (mg/L)	281	1.2	391	94	1470	<1	1140	615	1010	546	0.28	0.11
Manganese (mg/L)	11	16	<1	<1	51	4.0	32	33	32	30	3.5	<1
Nickel (mg/L)	61	<1	<1	<1	<1	<1	<1	<1	<1	<1	59	<1
Zinc (mg/L)	N/A	N/A	<1	<1	569	<1	81	<1	68	<1	0.35	0.03
[illegible]	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	68	2.7
Nitrate (mg/L)	NIA	NIA	N/A	NIA	NIA	NIA	N/A	NIA	N/A	N/A	9.1	<1

Table 2: Field System Dimensions and Removal Concentrations

AMD Type	Location	System Type	Surface Area m^2	Volume m^3	Flow	Retention Time	Acidity mg/L Before	Acidity mg/L After	Iron mg/L Before	Iron mg/L After	Sulphate mg/L Before	Sulphate mg/L After	Metals mg/L Before	Metals mg/l After
Ni/Cu	Central Ontario #1	Cells Flow hrough	224	188	0.9	145	139	27.5	13.3	7.6	2400	450	Ni 15.3	Ni 0.8
Coal	Nova Scotia #2	Cells Diffuse	100	40	0.3[a]	92.6	504	242	30.2	4.3	1213	920	Al 23.5	Al 12.i
Zn/Cu	Central Newfoundland #3	Cells Stagnant	12.5	34	-	151[b]	57.5	<1	(c)	(c)	202	27	Zn 23	Zn 0.7
Zn/Cu	Central Newfoundland #4	Bog Diffuse	44	22	14.7	1	431	217				489		
As/Ni	Northern Saskatchewan #5	Cell Stagnant	5.8	2.9	-	74[b]	(d)	(d)	2.2	0.06	264	40	Ni 26 As 9.3	Ni 2.6 As 0.9

(a) Estimated

(b) Time to onset of treatment used to calculate removal

(c) Metals not present in significant concentration

(d) < 10 mg/L in seepage

Table 3: Microbial Removal Rates

AMD Type	Location	Acidity Removal $g/m^3/day$	Iron Removal glm'lday	Sulphate Removal $g/m^3/day$	Metals Removal $g/m^3/day$
Cu/Ni	Central Ontario	**2.49**	**0.78**	8.60	Ni **0.17**
U	Central Ontario	**5.27**	**2.48**	**7.05**	(a)
Cu/Zn	Northern (22°C) Quebec	**8.01**	**3.06**	**11.82**	Zn **1.18**
Cu/Zn/Pb	Northern (22°C) Ontario	**48.62**	**39.29**	**50.71**	Zn **3.81**
Cu/Zn/Pb	Northern (5°C) Ontario	**11.35**	**5.52**	**17.50**	Zn **0.80**
U	Northern Saskatchewan	**4.07**	0.005	**15.89**	Ni As **0.17 1.81**
FIELD SYSTEM					
Ni/Cu	Central Ontario #1	**0.77**	**0.04**	**13.5**	Ni **0.10**
Coal	Nova Scotia #2	**2.83**	**0.28**	**3.16**	Al **0.12**
Zn/Cu	Central Newfoundland #3	0.37	(a)	**1.16**	Zn **0.15**
Zn/Cu	Central Newfoundland #4	**214**	**0.30**	**435**	Zn **71**
As/Ni	Northern Saskatchewan #5	(a)	0.03	**3.03**	Ni As **0.32 0.11**

(a) no metals present

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Passive treatment processes for the mineral sector

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ABSTRACT

Constructed wetland utilize a combination of neutralizing material and microbial activity as alternative to chemical treatment. These systems work well when the pH is above 4.5 and the acidity is less than 300 mg/L. Precipitation of metal hydroxide alters the hydraulic conditions which leads to failure. Anoxic limestone drains introduce alkalinity to AMD prior to treatment in the wetland system. Compost wetland promote microbial sulphate reduction. A summary of these systems is given.

Microbial systems (reactors and field tests) are reviewed. Long retention times and organic matter are required to maintain treatment. Passive treatments should be installed inside the waste management area Microbially active sediments serve to contain contaminants within the drainage basin to be decommissioned. Passive treatment can assist in polishing effluents when particulates are to be removed, utilising the surface area of attached macrophytes for adsorption. Design criteria and treatment capacity of passive systems are dependant on the biologically mediated reaction rates which are specific to the geochemical and physical conditions of the site. Examples are given of applications for decommissioning mining wastes.

INTRODUCTION

Sulphidic mining wastes oxidize and generate acid mine drainage (AMD). On many mine sites, this AMD generation will continue for thousands of years after the ore body has been depleted. Conventional treatment of AMD is effective but requires the addition of chemicals and operation of a chemical treatment plant in perpetuity. Secondary wastes (sludges) are produced which present a further environmental and economic liability. Passive biological keatment systems have received much attention as alternative treatments.

Mankind has utilized ecological approaches to treat domestic sewage and agricultural effluents for at least 2000 years (1). However, only since the early 1980's has the ability' of ecosystems to remove contaminants from wastewaters been exploited in the western world (2, 3, 4). Experimentation utilizing wetlands for the amelioration of Acid Mine Drainage (AMD) has been ongoing since the early 1980s in North America, after it was observed that coal seepages passing through natural wetlands emerge with a significant improvement in their characteristics (5).

The use of wetlands for the amelioration of AMD was evaluated in 1984, where natural wetlands, by default, received effluents from base metal mines located mainly in eastern Canada (6). As these wetlands were not designed for treatment of acid mine drainage, the study concluded correctly that none of the wetlands reduced downstream metal or acidity' loadings. The sediments in the wetlands were found enriched with metals, which indicated that metals were adsorbed onto the sediment. They were no longer active in removing metals. These conclusions were expected, since the wetlands were not designed to sustain the required biogeochemical processes which support the natural cleansing processes. The ecological approach to the utilization of wetland processes to ameliorate AMD in mining effluents bas been described (7).

Passive wastewater treatment utilizes natural purification processes which are based on chemical processes such as oxidation, reduction, coagulation, adsorption. absorption and the formation of precipitates. Biological factors which contribute to the treatment are microbial activities which mediate these chemical reactions. Physical factors which also have to be considered or can be utilized to assist in the process are gravity, light, aeration, dilution and wind-driven turnover (8). Wetland and lake sediments are the vessels in which these purification processes rake place.

This paper reviews the literature on anoxic limestone drains, aerobic and anaerobic constructed wetlands, compost wetlands and microbial systems. A discussion is provided on wetland design and the approach required to utilize passive systems particularly in decommissioning of mining wastes.

Aerobic Wetlands

Aerobic wetlands are generally dominated by emergent aquatic macrophytes, which are rooted in the wetland sediment. Cattails have been extensively planted in wetlands to treat coal AMD. These wetlands generally precipitate iron and manganese as the wetland provides oxidising conditions. The iron is removed as an iron hydroxide as the AMD passes through the wetland. The performance of three aerobic wetland systems is summarised in Table I. The systems are selected, as a reasonable number of performance characteristics are given, which was not the case for many systems reviewed in the literature.

Nine of the 14 TVA (Tennessee Valley Authority) constructed systems have been operating well for several years (9, 10). These wetlands treat AMD with relatively low Fe concentrations (0.7 to 69 mg/L, loading 0.03 to 6.13 g/day/m^2) and low net inflow alkalinity (35-300 mg/L equivalent of calcium carbonate). Effective removal of Fe takes place, and to a lesser extent Mn. Data on the hydrological characteristics of the wetlands required to assess the potential effects of groundwater contributions, evapotranspiration, and precipitation are frequently not available.

Table I - Performance Data for Aerobic Wetlands

System	Impoundment 1		Tracy-large		Tracy-small	
Reference	(9)		(10)		(10)	
Water	Coal drainage		Coal drainage		Coal drainage	
Size (sq. m)	5700		420		108	
Flow rate (L/min.)	73		30-57		23-30	
Retention time (d)	NIA		3.8-7.5		1.9-2.5	
Age for data (mo)	0-72		0-12		0-12	
Substrate	NIA		NIA		Limestone/peat	
Plants	*Typha*		*Typha*		*Typha/Carex*	
Location	Inflow	outflow	Inflow	outflow	Inflow	outflow
pH	6.1	6.7	2.7	2.6	3.1	2.8
Sulphate (mg/L)	NIA	NIA	2618	2683	1560	1551
Aluminum (mg/L)	NIA	NIA	178	180	41	46
Iron (mg/L)	69	0.9	284	271	149	94
Manganese (mg/L)	9.3	1.8	1.5	1.7	1.2	1.3

Four of the TVA systems, characterised by low or zero input alkalinity and high Fe loadings (40-170 mg/L, 5-41 g/day/m^2), have failed to meet discharge requirements (Table I). Sphagnum bogs have also been tested for their ability to treat AMD (11) but their performance has not been promising. The Tracy wetlands in Montana (12) were constructed with a substrate of limestone and soil with a peat cover. Over the first year of operation, both wetland systems failed to improve the quality of two coal acid mine drainages. This was attributed to inadequate retention times.

The effectiveness of these aerobic wetland systems was found to be very variable and generally only worked well where the pH of the water was initially high. Failure may be attributed to inadequate hydrological conditions (channelling, short retention times, leakage). Over a period of years, the iron precipitation will result in the build-up of sludges which will require removal for a continued operation of the wetland. Such build-up has not been well documented and most papers to date discuss the performance of wetlands only 3 years old or less.

Brodie et al. (9, 10) described the design of wetlands to treat coal AMD in the TVA area to meet compliance for Fe and Mn concentrations as well as pH. Local materials (soil, gravel, fly-ash, etc.) were used in the construction, and cattails transplanted by hand. The substrates often have low permeabilities and therefore the AMD was mainly treated in surface water flow. This promoted the oxidation and hydrolysis of iron, leading to the build-up of ferric hydroxide. Since water is prone to chamel-flow, low retention times and the utilization of only a small part of the wetland resulted

Anoxic Limestone Drains

Anoxic limestone drains (ALDs) have been constructed in the U.S., principally to add alkalinity and increase pH to the acid mine drainage water from coal operations prior to passage through a wetland. These systems comprise a buried trench of high grade limestone chips over an impervious liner which is covered with a clay layer. They are designed for passage of water through the limestone while maintaining the iron in the reduced or ferrous state. If the iron is exposed to oxygen, it will oxidize and precipitate as ferric hydroxide if the pH exceeds 3.5.

Anoxic limestone drains utilize limestone to release alkalinity nuder anoxic conditions. Carruccio and Geidel (13) first used this principle for emerging seepages which, after contact with limestone, returned into the tailings pile. Drains were subsequently used as a pre-treatment to wetlands, notably in coal mines in the TVA region. The performance of three selected anoxic limestone drains is summarised in Table II.

Table II - Performance Data for Anoxic Limestone Drains

System	Morrison		Shade		Impoundment 4	
Reference	(14)		(15)		(16)	
Water	Coal drainage		Coal drainage		Coal drainage	
Size (cubic. m)	30		130		450	
Flow (L/min)	7.5		15		130	
Retention time (d)	0.83		1.81		NIA	
Age for data (mo)	0-13		0-12			
Location	Inflow	outflow	Inflow	outflow	Inflow	outflow
Alkalinity (mg/L)	15	255	0	103	0	100
Acidity (mg/L)	438	83	194	0	350	40
pH	4.7	6.2	3.4	6.6	3.1	6.3
Sulphate (mg/L)	1332	1168	943	I300	NIA	N/A
Aluminum (mg/L)	0.6	0.2	22	5	NIA	NIA
Iron (mg/L)	208	168	4	1	6	1
Manganese (mg/L)	44	46	35	36	1.6	0.2

N/A Not available

The Impoundment 4 system at Fabius, Alabama, described by Brodie et al. (16), was constructed to treat a coal drainage prior to its passage through a constructed wetland. It worked well for 6 months with a precipitous drop in Fe and Mn concentrations in the effluent. Acid mine drainage may contain both ferrous (oxidized) and ferric (reduced) iron which precipitate around pH 5.5 to 6.5 and pH 3 to 4 respectively. If the pH in the drain is low, ferric hydroxide precipitates will be produced which can rapidly reduce the hydraulic conductivity of the limestone and render the system useless. Replenishment of the limestone would require extensive excavation, In the Impoundment 4 drain, such a build-up of $Fe(OH)_3$ precipitates took place which eventually blocked the flow.

The drains described by Nairn et al. (14, 15) and by Hedin et al. (17) set up in 1990, located in the southern Appalachians, were effective in providing alkalinity. The seepage in the Morrison system gained alkalinity for the 12 months following construction. The water leaving the drain then passed through a wetland in which more than 99% of the iron and 60% of the manganese were removed. *This* system worked effectively for the reported period.

At Shade, excellent alkalinity generation was observed (15). In this system, however, the drain reduced Al concentration considerably. Aluminium hydroxide precipitates at pH > 3.5 to 4.5 and thus may build up in the drain in the long term. All anoxic limestone drains are expected to eventually become ineffective due to precipitate clogging or through dissolution of the limestone. To date, the literature gives no reasonable estimates of the expected effective life of these systems. After several years experience with ALDs, the clogging problems have led to the recommendation of using pipes of wider diameter and using limestone of larger particle size (18).

Comaost Wetlands

Compost wetlands evolved from aerobic wetlands to treat AMD. These approaches attempt to promote the sulphate reducing bacteria which can both generate alkalinity, raise the pH and result in the precipitation of heavy metals as sulphides in the growth substrate layer. These wetlands generally use substrates such as spent mushroom compost to which limestone added. This limestone and the compost raises the pH and releases alkalinity. This complicates the quantification of the contribution of sulphate reduction to the treatment process. The performance of some compost wetlands are summarised in Table III.

Table III - Performance Data for Compost Wetlands

system	Simco #4		Kentucky		Kentucky		Big Five Tunnel		Big Five Tunnel	
Reference	(19)		(20)		(20)		(21)		(21)	
Water	Coal drainage		Coal drainage		Coal drainage		Base metal AMD		Base metal AMJJ	
Size (sq. m)	2623		180		180		18.3		18.3	
Flow rate (L/min)	328		5.9		59		3.8		3.8	
Retention time (d)	4.2		5.1		5.1		3.4		3.4	
Age for data (mo)	0-48		0-25.6		0-25.6		0-36		0-36	
Substrate	Limestone/mush.comp.		Peat		Mushroom compost		Mushroom compost		Peat/manure/sawdust	
Plants	*Typha*		*Typha*		*Typha*		5 species		5 species	
Location	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Oufflow	Inflow	Outflow
Alkalinity (mg/L)	87	26	0	0	0	0	NIA	NIA	NIA	NIA
Acidity (mg/L)	123	32	557	559	557	189	NIA	NIA	NIA	NIA
pH	6.5	6.4	2.9	2.8	2.9	3.4	3.0	4.6	3.0	3.6
Sulphate (mg/L)	1146	1067	3132	3169	3132	2644	NIA	NIA	NIA	NIA
Aluminum (mg/L)	NIA	NIA	27	31	27	11	NIA	NIA	NIA	NIA
Copper (mg/L)	NIA	NIA	NIA	NIA	NIA	NIA	.74	.23	0.83	0.6
Iron (mg/L)	111	42	119	93	119	27	40	25	38	21
Manganese (mg/L)	NIA	NIA	19	22	19	15	30	31	29	30
Zinc (mg/L)	NIA	NIA	NIA	NIA	NIA	NIA	9.1	4.9	9.2	7.2

NIA not available

The Simco #4 Wetland (19, 22) has been successful in the removal of iron from coal AMD over a period of 8 years. This system had a substrate of 15 cm of crushed limestone overlain with 45 cm of spent mushroom compost. These conditions are similar to an anoxic limestone drain. Following construction. the effectiveness of the system improved over two years. Performance was then variable (negatively correlated with flow) but showed a clear improvement after the placement of hay bale dikes which reduced water short-circuiting (Table III).

The Big Five Tunnel system in Colorado (21) treats a seepage which has an average pH of around 3, 1 mg/L Cu, 35 mg/L Fe, 30 mg/L Mn and 10 mg/L Zn. The wetlands are relatively small, comprising five different treatment cells. The substrates used in the cells are various mixtures of mushroom compost, peat, manure and wood shavings overlying *IS* cm of limestone, all substances which neutralise acidity and adsorb metals, Performance of the system was very variable during the summer months with a poorer performance during the winter months for all measured parameters. The nument-rich organic material would definitely encourage microbial activity of sulphate and iron-reducers, but this treatment process cannot be differentiated from the effect of the limestone and mushroom compost added to the cells.

The work of Wieder (20) is the best-documented wetlands application to treat AMD. Five wetlands in Kentucky were constructed with 5 different substrates and operated for 111 weeks with weekly monitoring of effluent parameters. The mushroom compost wetland (containing limestone) gave the best performance while the peat wetland performed the worst.

The wetlands did not improve the effluent in the winter and failed to recover after the second winter. During the two summers, titratable alkalinity was generated in the mushroom compost and straw/manure wetlands. The alkalinity generated is attributable directly to dissolution of limestone. The reduction of sulphate in 4 of the 5 wetlands indicates that microbial sulphate reduction may also account for pH improvement and alkalinity generation. Towards the end of the study the acidity load from the seepage overwhelmed the ability of all wetlands to generate alkalinity and remove metals. A modified compost wetland where coal mine drainage passes up through a sulphate reducing, limestone enriched spent mushroom compost sediment following oxidation (to remove iron) has recently been described (23).

Microbial Reactor Systems

Unlike the compost wetlands, system based on microbiology attempt to provide optimum conditions for the bacteria through system design. Unfortunately some of the published work has once again used additions of limestone to the bacterial growth substrate, as it is generally believed that sulphate reduction requires pH above 4. During the development of the Budelco process for sulphate treatment it was reported that sulphate reduction can function at pH values of less *than* 4. (24). Therefore, such systems would not require limestone replenishment. However a continued source of nutrients for the bacteria is required. This could be achieved through regular (annual) addition of suitable, biodegradable materials or through providing a living cover over the microbially active sediment, which in the long term provides organic matter through plant decay (25).

Reactor system have been set up to test the ability of sulphate reducing bacteria to generate alkalinity and precipitate metals from AMD. Small-scale flow-through and large-scale (200 L or more) batch reactors (25-29) have established that metal removal and alkalinity generation can occur (Table IV). In the Kuyucak et al. (27, 29) and Dvorak et al. (26, 28) reactors, limestone was added which makes quantification of the relative roles of bacterial sulphate reduction and limestone dissolution difficult. It was established that in the presence of organic amendment alone, substantial amounts of alkalinity can be generated (25). Nickel concentrations are reduced from 60 mg/L to less *than* 1 mg/L and iron from 280 mg/L to 1 mg/L. These reactor experiments indicate that treatment can be achieved if a batch configuration can be designed. Since the AMD is more acidic, reaching acidity of 4000 mg/L as tested from a site in Northern Quebec, the time until treatment is achieved is considerably longer.

Table IV - Performance Data for Microbiological Systems

System	Pittsburgh		Palmerton		Mattabi		Makela		Denison		N.Quebec	
Reference	(26)		(26)		(27)		(25)		(25)		Boojum unpub.	
Water	Coal drainage		AMD		AMD		AMD		AMD		AMD	
Flow (L/min)	0.06		0.07		0.0001		Static		static		static	
Retention time (d)	5		17		7		65, 120		104		500	
Age for data (mo)	1-12		1-5		0-1		8-20		0-4		0-16	
Substrate	Mushroom compost				Limestone/pyruvate		Flax		Flax		Flax/alfalfa	
Location/time	In	Out	In	Out	In	Out	Before	After	Before	After	Before	After
Alkalinity (mg/L)	0	349	17	1583	NIA	NIA	146	3035				
Acidity (mg/L)	201	15	520	1	N/A	N/A	1197	301	1014	382	4250	405
pH	3.2	64	6.2	7.1	3.3	62	5.3	7.0	3.3	58	2.4	72
Sulphate (mg/L)	NIA	NIA	NIA	NIA	4000	2275	3663	567	879	33	5760	87
Cadmium (mg/L)	N/A	NIA	NIA	NIA	24	0.06	NIA	NIA	NIA	NIA	2.1	<1
Iron (mg/L)	53	8	NIA	NIA	133	91	281	12	391	94	1470	<1
Manganese (mg/L)	NIA	NIA	26	0.5	NIA	NIA	11	16	<1	<1	51	4
Nickel (mg/L)	N/A	NIA	0.9	0.02	NIA	NIA	61	0.6	<1	<1	<1	<1
Zinc (mg/L)	NIA	NIA	317	03	NIA	NIA	NIA	NIA	<1	<1	569	<1

N/A not available

A pre-treatment step for such effluents has to be considered, as the retention time required would make a passive approach impracticable. Batch treatments with long retention times are required to optimise conditions for sulphate reduction and other microbial alkalinity generating processes.

Constructed Sediment Systems

The results from the reactors essentially simulate conditions for anaerobic alkalinity generating processes which occur in nature in sediments of wetlands and lakes. In constructed sediment systems, microbial decomposition in the sediments of the organic material release organic acids to the water column, which complex or bind the metals, converting them to particulates. The particulates settle to the sediment, where further decomposition will stimulate sulphate reduction. In the appropriate pH/Eh conditions, the metals are then biomineralized in the deeper portions of the sediment.

Kalin (25, 30) tested the use of a floating vegetation mats to extend the sediment conditions through the water column. A test cell system was installed for the treatment of AMD from the Copper Cliff tailings in Sudbury, Ontario (25). The final configuration of the system, a microbially-active sediment with a floating vegetation cover, produced, with a retention time of 131 days, a removal of 80-87% of the nickel load, 77-98% of the copper load, 10-20% of the sulphur loading as well as 47-73% of the acidity load in its first year of operation at a flow of 1 to 2 L/min.

Removal rates of the microbial sediment treatment approach, referred to as ARUM (Acid Reduction Using Microbiology) are presented for several test systems for several AMD types tested in the field in Table V. The system types are described as either "cells" where sediments are constructed with organic matter or "Bog" where an existing bog sediment was supplemented with organic matter. The removal rates of these systems are calculated, using the time it required to remove the contaminant from a given volume of water which is exposed to a given area of microbially active sediment. The rates can then be expressed as either mg removed /m^3/day or can be calculated as mg removed/m^2 of sediment/day. The relatively large ranges of removal capacity are determined by the different chemistries of the AMD which is treated. Thus removal rates for sulphate can range from 0.3 mg/m^3/day to 22 mg/m^3/day (Table V).

A recent feasibility study was completed examining the use of ARUM in an existing bog which was part of the waste management area, as it is located between a waste rock pile and an open pit, both to be decommissioned. The waste rock pile generates seepage which could be diverted into the bog, which represents a perched water table. Field and laboratory reactor experiments yielded removal rates ranging from 154 to 253/mg/m^2/day for Ni and 196 to 211 mg/m^2/day for As (35, 36). The bog area available for treatment is well above that area required to treat the annual contaminant load from the seepage generated by a waste rock pile. Thus the process could be utilized, replacing the requirements for collecting and pumping the seepage to a treatment facility in perpetuity.

Bioloeical Polishing

Biopolishing is a process in which surfaces are provided such that algae can attach to them and grow floating in the effluent to be treated. This process exploits ability of algae to serve as a biosorption surface which, through their continued growth, provide new surface areas. Candidate algal groups includes those species that excrete polysaccharide sheets on their cell walls, which protect them from the toxic effect of the high metal concentrations in the effluentto be treated. Thus, metals are complexed onto the cell walls of algae or moss which grow on the surface material added in the polishing ponds.

The algae also collect precipitates (mainly Fe and Al hydroxides) which are formed in the effluent when the appropriate geochemical conditions are created in the polishing pond. As the algae grow continuously, new algal surfaces are created for polishing. Growth rates are controlled by the availability of nutrients in the effluent and the temperature. Therefore, performance of biological polishing processes is reduced during winter months.

Table V - Constructed Sediments, Field Performance

AMD Type	System	Period/ retention time days	Volume m^3	Acidity removed $mg/m^3/day$	Sulphate removed $mg/m^3/day$	Iron removed $mg/m^3/day$	Metals removed $mg/m^3/min$
Base metal(a)	Cells 3 & 4	173	188	0.43	5.76	(b)	0.65 (Ni)
Coal	Bog	454	0.6	0.178	0.322	0.011	(c)
coal	Cells	55	40	7.1	22.2	0.29	(c)
Polymetallic	Cell	151	34	NIA	NIA	N/A	0.33 (Zn)
	Bog	3.6	53	2.94	1.22	N/A	1.36 (Zn)

(a) Based on data for 5 sampling dates in 1992 - 1994 with a flow rate of 0.1 to 1.5 L/min

(b) Iron (>95 % of 250-350 mg/L) removed in oxidation/precipitation cells prior to passage through Cells 3 & 4

(c) Metals not present in significant concentration.

N/A Not available

The ponds in which biological polishing is to be used have to take into account the performance of algae during the winter months which leads to over performance in the summer months. Biological polishing has been implemented as a full scale treatment process for the removal of Zn (31) and Ra^{226} (32 and 34). This process has been shown effective in containing the contaminants within the polishing ponds, treating volumes of effluents of up to 20 L/sec for Zn removal. Biological polishing is used to reduce the total load of Ra^{226} leaving a drainage basin by about 40 %.

DESIGN CRITERIA FOR PASSIVE SYSTEMS

Initial guidelines for the construction of wetlands were based on the performance of systems operating in the Tennessee Valley Authority (TVA) region (9). Wetland size is based on the estimated area to remove a specific quantity of iron to an acceptable level. The guidelines have changed as new data became available (Hedin et al., 1994).

Hedin and Nairn (34) have suggested criteria for selection of wetland type (aerobic or compost) and sizing based on data from a variety of constructed wetlands for mine drainage treatment. Where the water is net-alkaline, passive systems with aerobic wetlands are recommended with sizing based on 20 $g/m^2/day$ Fe or 0.5 $g/m^2/day$ Mn. For net-acidic waters, systems with compost wetlands are recommended with sizing based on 5 $g/m^2/day$ acidity and 0.5 $g/m^2/day$ Mn.

The performance data from the microbial systems, both the reactors and the field systems where constructed sediments were tested, indicate that effectiveness of the treatment is dependant on the rate of the microbial reactions which are governed by the type of effluent to be treated and the time available for treatment. The use of passive systems for a waste stream is determined by the hydrological and geochemical conditions of the waste management area. Field tests of the effluent to be treated have to be carried out to give removal rates specific to the effluent and the site conditions. Those removal rates are translated into g/m^2 of contaminant removed/m^2 of sediment area/per unit time. The feasibility of the use of the passive system is then determined by the annual contaminant load to be treated and by the area available for treatment. The same approach has to be used for biological polishing systems. Thus, design of a passive treatment system requires site-specific field tests which yield design criteria.

CONCLUSION

The literature review revealed that many of the published performance data are derived from experimental systems. Emphasis was placed frequently on the removal of selected elements. The pollutant concentration of influent and effluent parameters were reponed. Only for a limited number of sites were data reported which would allow assessment of loadings which would lend themselves to derive reliable design criteria.

Anoxic limestone drains can initially release much alkalinity but, in the presence of heavy metals, they are likely to become clogged up with iron and aluminum hydroxides.

In all systems, metals are removed through precipitation, and sludges will accumulate and eventually require removal. Most passive treatment systems described in the literature have been operating for a shon period of time and, with the exception of anoxic limestone drains, problems associated with build-up of precipitates are not well documented. Such build up however leads to alteration of the hydrologic characteristics of the wetlands and coverage of surfaces of organic materials, rendering them unavailable for both biosorption processes or as substrates for decomposing microorganisms required for sulphate reduction. In the *ARUM* configuration for a tailings seepage rich in iron, an iron hydroxide precipitation cell was installed, preceding the *ARUM* treatment cells (25, 30).

Conventional wastewater treatment plants are designed for the removal of specific contaminants and at particular loading rates, utilizing chemical process reactions which take place at defined rates. Physical forces are used to remove the resultant precipitate. Energy is required to support any treatment process. In passive treatment systems, the wetland plants, through photosynthesis, serve as an energy source, generating the required organic matter for the sediment-bound processes to sustain the treatment system. The summary provided on microbial reactors and constructed sediments indicates that passive systems require sufficient retention time for the microbially-driven reactions. Microorganisms mediate oxidation/reduction reactions in anaerobic conditions. For example, the rate at which sulphate reducing bacteria operate to reduce sulphate to sulphide using, as an oxidant (electron donor), organic acids, is closely linked with the rate at which these compounds are produced through the decomposition of plant or other organic matter, a process mainly driven by aerobic microbial processes at the sediment-water interphase. The precipitation of sulphide with metal ions or its release to the atmosphere as hydrogen sulphide represents a purification step. Wieder (20) studied in some detail the form of sulphur, iron and other metals in wetlands. The iron was present in an exchangeable form, organically bound or as a carbonate or hydroxide. Carbonates and sulphides were more abundant in the mushroom compost and straw manure wetlands than in peat only wetlands.

Passive treatment systems are incorrectly perceived as systems with no requirement for power or maintenance, and frequently as a "do nothing" option. This summary of the passive treatment approaches do require a power supply in the form of sunlight to generate organic matter, which otherwise has to be added. They do require minimal ongoing maintenance to assist the water treatment process, which can be self-sustaining if an appropriate nutrient supply is present. Without the results of the various experiment approaches it would not have been possible to define the criteria required to utilize passive treatments in the mineral sector. In decommissioning plans, several sites in Canada have opted to apply the passive approach, and chemical treatment has not been required to date.

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